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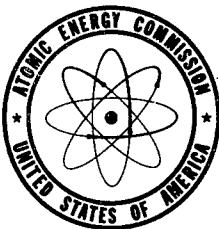
SUMMARY REPORT ON THE DETERMINATION  
OF IMPURITY ELEMENTS IN AMES THORIUM  
BILLET A-520

By  
J. P. Burelbach  
R. J. March

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September 1953

Argonne National Laboratory  
Lemont, Illinois



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ARGONNE NATIONAL LABORATORY  
P. O. Box 299  
Lemont, Illinois

SUMMARY REPORT ON THE DETERMINATION OF  
IMPURITY ELEMENTS IN AMES THORIUM BILLET A-520

Compiled by

J. P. Burelbach and R. J. March

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ABSTRACT

A representative billet of Ames thorium metal has been analyzed for impurity elements by the nine laboratories participating in the thorium analytical program of 1952-53. Chemical and spectrographic results and procedures are presented, together with a summary of the program meeting of September 1952 and post-meeting comment. Also included is the result of a danger coefficient test in which the Ames metal was compared with iodide thorium in the CP-2 reactor of the Argonne National Laboratory.

## SECTION I. SUMMARY

Introduction

Corrosiveness, hardness, and cross-section are among the chief criteria for selecting high quality thorium metal for reactor application. These qualities, in turn, are dependent upon the type and concentration of impurity elements present.

Early in 1952, the need for reliable methods of analysis for specification of Ames grade thorium metal became apparent. An analytical program was therefore established under the sponsorship of the Chicago Operations Office of the Atomic Energy Commission.

Two billets of Ames virgin metal, each weighing ca. 94 lb., were set aside to provide homogeneous samples of thorium chips and solid bar samples for distribution to interested laboratories throughout the AEC.

Of the nineteen installations receiving samples of thorium, the following were able to contribute analytical data for the thorium analytical meeting which was held at the Argonne National Laboratory in September, 1952:

Ames Laboratory

Argonne National Laboratory (ANL)

Battelle Memorial Institute (BMI)

Horizons, Inc.

Knolls Atomic Power Laboratory (KAPL)

Massachusetts Institute of Technology (MIT)

National Lead Company (NLC)

New Brunswick Laboratory (NBL)

Oak Ridge National Laboratory (ORNL)

This report summarizes the work of the above participants in the analytical program.

The more important impurity elements found in Ames Billet, A-520, together with the "averaged" concentration values are listed below. In general, there was good agreement among the laboratories for most of these elements. Values enclosed in parenthesis, however, indicate that inconsistent or insufficient quantitative results were reported.

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Aluminum	10	Lanthanum	4
Boron	0.4	Magnesium	(10)
Beryllium	70	Manganese	2
Cadmium	0.1	Neodymium	6
Calcium	15	Nickel	27
Carbon	390	Nitrogen	60
Cerium	25	Oxygen	1100
Chromium	10	Silicon	< 50
Copper	4	Uranium	2
Hydrogen	(10)	Zinc	(4)
Iron	60	Zirconium	(400)

Only 3 laboratories reported rare earth values; a number of these were at the limit of detection. Such rare earth elements as dysprosium, gadolinium, europium, and samarium have a considerable effect on the total impurity absorption cross-section even at the detection limit. This is also true in the case of cobalt, indium, and lithium.

To check for any gross errors in the computed impurity cross-section, a danger coefficient test was run in the CP-2 reactor at Argonne. If the iodide thorium metal, which was used as reference material, can be assumed to be free

of the high neutron-absorbing elements mentioned, then the calculated Ames metal impurity cross-section of  $0.137 \text{ cm}^2$  is a very conservative result.

On the following pages of this section, comments made at the analytical meeting, as well as post-meeting information, is summarized.



### ALUMINUM

In the analysis for aluminum, the only value obtained by direct chemical means is that reported by MIT, using the fluorometric method. This value is somewhat higher than results obtained by use of the spectrograph. The Ames spectrographic method has been checked in the past by the Ames spectrophotometric method. It was found that the 2 methods yielded results which were in close agreement.

The spectrographic methods are given in detail in Section IV. Briefly, ANL, NLC, and NBL used the carrier distillation technique. KAPL and ORNL first extracted the thorium. KAPL then evaporated the concentrated raffinate on an electrode while ORNL used the porous cup method. Ames employed the conducting briquet technique for all elements except boron, cadmium, and zinc. For these the carrier distillation method, because it possesses a greater sensitivity for these elements, was used.

The laboratories reporting spectrographic values, with the exception of Ames and ANL, allowed reagents to contact the samples. This, of course, can be a source of error unless proper reagent blanks are run.

The high value obtained by NLC is attributed to a contamination problem that they have experienced with aluminum. In addition, Lindsay Light and Chemical thorium nitrate was used to prepare the matrix material. ANL has found that this material can give a high aluminum blank of about 20 ppm. This, in fact, controls the detection limit for this analysis at ANL.

Reasons for the KAPL variation are not as apparent. The KAPL value is obtained from a single sample which was analyzed as a concentrated sample and in 2 dilute samples. The concentrated sample gave a value of 15 ppm, whereas the dilute samples yielded 22 and 28 ppm. The detection limit

with the dilute samples was poorer by a factor of ten. Hence, there is a possibility that a value lower than 22 ppm is indicated.

#### BERYLLIUM

The results of spectrographic analyses for beryllium indicate that comparative values are obtained by 3 different methods. NBL found a high value of the order of 300 ppm Be, which is not reported as due to known beryllium contamination. KAPL did not report a value because the beryllium lines were too dark to read accurately.

#### BORON

Values by chemical methods are reported by ANL, NLC, and NBL. In each laboratory the boron is distilled as methyl borate, the boron content being determined by the use of tumeric as the chromogenic agent. ANL employs hydrochloric acid only in the dissolution of the sample, while nitric and hydrochloric acids are used at NLC. NBL uses nitric and hydrochloric acids plus a trace of fluoride. In each NBL sample a white residue remained after acid treatment. This residue was filtered, washed free of acid, covered with 0.1 N calcium hydroxide, and evaporated to dryness. The sample was then washed, treated with boron-free sodium carbonate, and carried through all steps of the procedure. Boron was not detected in this residue.

The spectrographic analysis of boron is complicated not only by the contamination problem but also by the volatilization behavior of the oxide and spectrographic line interferences.

It was the experience of the majority of the laboratories that unless a quartz-lined muffle furnace be used for the ignition of the metal to the oxide, there is a great possibility of boron contamination. Results which

are high by a factor of ten were obtained by BMI when the oxide sample was not prepared in a quartz-lined muffle. NBL has found it advantageous to use a special quartz-lined furnace exclusively for the boron determination. It was pointed out by MIT that contamination is also likely to occur when new platinum boats are used without prior cleaning.

The problem of ignition losses has been studied in some detail by Ames. It has been observed that the fraction of boron volatilized from a matrix material which does not fuse can be markedly influenced by the chemical, physical and crystalline constitution of the matrix and associated impurity. Ames reports that when the metal sample is ignited in air to form the oxide, losses of boron amounting to 56% were obtained, whereas losses of boron amounting to 78% were reported when the dissolution procedure was used. The Ames result of  $0.34 \pm 0.02$  ppm boron represents the average of values for three 1 g samples of chips oxidized in air and three 1 g samples of chips converted to oxide by the dissolution method. These results are corrected for differences in volatilization behavior and also for thorium line interference in the spectrographic analysis.

In addition to the effect of sample preparation upon boron losses, muffle furnace temperature and oxidation time must also be considered. NLC found that losses can be increased by using higher oxidation temperatures and/or longer ignition periods. Excessive losses in the oxide preparation will, in consequence, make it more difficult to obtain a reliable boron impurity value.

#### CADMIUM

The concentration of cadmium in the thorium sample is indicated to be of the order of 0.1 ppm. Spectrographic results in this range are complicated by the high ignition loss of cadmium due to its ease of volatilization. Ames has observed losses greater than 95% by either the direct oxidation method or the oxide dissolution procedure. The BMI colorimetric determination falls in line with the spectrographic results.

#### CALCIUM

In the calcium determination, the ANL value is believed to be reliable only within a factor of 2 due to a high lower limit of detection. This lower limit is 20 ppm and is controlled by the residual calcium in the thorium matrix. The ORNL result is considerably higher than the other values reported. The reason for this variation was not determined.

#### CARBON

Each of the 9 laboratories obtained values for carbon. The thorium samples were oxidized either by Globar ignition at temperatures between 1150°C and 1300°C, or by induction ignition at temperatures in the range of 2500-3000°C. In a majority of cases about a 2-gram sample of chips was analyzed in the "as received" condition.

Five results obtained by Globar ignition ranged between 360 and 417 ppm. Two separate ORNL samples, which averaged 380 ppm, analyzed individually to 220 and 540 ppm, giving a large deviation. The BMI and Horizons values of 330 and 577 ppm, respectively, were obtained using samples of 0.25 to 1 g.

It was the experience of MIT that at temperatures up to 1200°C incomplete combustion resulted. At 1300°C, consistent values were obtained; apparently complete combustion was achieved. ANL, however, obtained consistent results at 1150°C.

High frequency induction heating was used by Ames, BMI, and KAPL. Ames and KAPL both obtained low values by this technique. A recheck by Ames indicated that their absorbant was poor. With a new absorbant, 3 determinations yielded an average value of  $410 \pm 10$  ppm, a value comparing favorably with BMI's induction result and with most of the Globar ignition values.

It was suggested that a possible cause for the low KAPL value may be incomplete combustion brought about by the formation of sintered oxide at the high induction heating temperatures. In the Ames procedure, this effect is less likely to occur, since the chips are ground to minus 20 mesh before oxidation of the sample.

#### CHLORINE

In the analysis for chlorine, both ANL and MIT noted a large spread in their results. ANL suggested that this variation may be due to segregation of chloride in the sample.

The ANL results were obtained using Pyrex equipment, whereas MIT used platinum ware. ORNL pointed out that chloride contamination may occur when sample dissolution is done in Pyrex.

#### CHROMIUM

Results for chromium by colorimetric and spectrographic methods were in good agreement. The two laboratories submitting colorimetric data employed diphenylcarbide in their procedures.

### COPPER

Consistent results were reported for both colorimetric and spectrographic methods. Diethyl dithiocarbamate was used to obtain the two colorimetric values. In the spectrographic analyses, the original high value of 15 ppm reported by BMI was discarded in favor of their second value of 6 ppm. This value was determined along with the boron and iron recheck, using a silica-lined muffle to oxidize the sample.

In the analysis of the solid sample, NBL had 2 contaminated samples which yielded high copper values. These values were omitted in the reported average value.

### HYDROGEN

The hydrogen values reported gave an estimate of the hydrogen present in the sample on a moisture-free basis. Several laboratories pointed out that the methods which were used for detecting hydrogen do not measure the absorbed water, and the given results must therefore be considered as minimum values.

BMI found the tin-fusion method to be superior to their vacuum fusion method for hydrogen under the circumstances of high relative oxygen content. Erratic results for hydrogen ranging around 1 ppm were found by the vacuum fusion method.

In the tin-fusion analysis the extracted gas is much richer in hydrogen (80-100%). Sensitivities as low as 0.2 ppm  $H_2$  have been obtained for a 5 g sample. A limited number of tin-fusion analyses on thorium have been performed at BMI; as yet the individual variation in results cannot readily be explained.

### IRON

Seven colorimetric and 5 spectrographic results are reported. The values range from about 50-70 ppm for each method of analysis. The ortho-phenanthroline method with hydroxylamine as reductant was the colorimetric method generally used. MIT, however, employed hydroquinone as the reductant instead of hydroxylamine. BMI was the only laboratory reporting an iron determination by the thiocyanate method.

In a recheck of their spectrographic value, BMI obtained an iron value of 55 ppm, about 15 ppm lower than the value originally reported.

### LEAD

Three spectrographic values for lead varied from about 1 to 5 ppm. The 2 other values reported were <1 by NLC and 11 ppm by KAPL. The lower limit of detectability at KAPL was 4 ppm which may account for their high value. The lower limit at ANL was 1 ppm, and at BMI the limit was 2 ppm. No explanation was given for the variation of ORNL's polarographic value from the spectrographic data.

### LITHIUM

Two spectrographic values and a single flame photometer result all yielded a value of less than one ppm for lithium.

### MAGNESIUM

Three laboratories reported spectrographic values of 3, 10, and about 15 ppm. ANL could not find magnesium at their detection limit of 10 ppm set by the residual impurity in their matrix material. Using the same grade of thorium nitrate for their standard, NLC obtained a value of 15 ppm.

#### MANGANESE

Four colorimetric and 7 spectrographic results are reported and appear consistent. In the colorimetric determination, Ames, BMI, and NBL employ periodate to oxidize the manganous ion while ANL uses peroxydisulfate. Detection limits in the spectrographic determinations are about 0.5 - 1 ppm for three laboratories. ORNL reports a limit as low as 0.1 ppm.

#### MOLYBDENUM

The single colorimetric result is a 2 ppm value reported by BMI using the thiocyanate procedure. A spectrographic value of <10 ppm is reported by ANL, and <2 ppm is given by BMI. For this determination, BMI used a concentration method prior to spectrographic analysis. The method involves a co-precipitation of molybdenum sulfide with copper sulfide as carrier.

#### NICKEL

The four colorimetric results which are reported vary from 26-29 ppm. Dimethylglyoxime was used in the color development at ANL and BMI. Diethyl dithiocarbamate was employed at ORNL. Ames used 1,2-cycloheptanedionedioxime.

In the spectrographic determinations, four results vary from 20-35 ppm. Two high values of > 50 and 52 are reported by NLC and NLB, respectively, and may be explained as due to high blanks. NBL estimated that their blank was about 20 ppm.

#### NITROGEN

All laboratories performed one or more Kjeldahl analyses. Seven results were in the 50-70 ppm range, and 5 of these fell within  $60 \pm 5$  ppm. The ORNL result of 110 was supplied as post-meeting information. The reason for its variation was not determined.



The thorium samples were, for the most part, run "as received." Ames, however, cleaned their sample with 8 N  $\text{HNO}_3$  and 6 mg of  $\text{Na}_2\text{SiF}_6$ . It was suggested that this may be responsible for their somewhat high result. The Ames data included 2 recheck values done by the Ames procedure which resulted in  $71 \pm 1$  ppm.

In the Horizons procedure, by which a 20 ppm value was obtained, fluoride ion was not used in the dissolution of their sample. ANL had tried to dissolve their sample without fluoride and obtained a low result of 35 ppm. Another factor contributing to the low Horizons result may have been sample losses due to repeated evaporations to dryness.

At KAPL, a small amount of boric acid was used to tie up the fluoride. After steam distillation, the colorimetric technique was used rather than titration.

The procedure generally employed by the laboratories was as follows. About a 1 g sample was dissolved in 6 N  $\text{HCl}$  with a trace of  $\text{HF}$  or complex fluoride ion. After digestion, sodium hydroxide solution was added and a steam distillation performed. The condensate was collected in ca. 2%  $\text{H}_3\text{BO}_3$  and titrated with ca. 0.01 N  $\text{HCl}$  using a suitable indicator.

The vacuum fusion results were in fair agreement considering the difficulties involved in the analytical procedure. No correction for recovery was made in the KAPL analyses, hence their values are expected to be low.

#### OXYGEN

Six laboratories performed the insoluble residue test expected to give a relative measure of the oxide present in the metal. In general the residue was obtained as  $\text{HCl}$  insoluble or perchloric acid insoluble.

At MIT, difficulty was experienced in filtering the perchloric acid residue; with the HCl procedure, a black sludge was obtained which remained even after prolonged heating. To remove the blackness, a trace of hydrofluoric acid was added. A value of 820 ppm was obtained. This value was lower than any other value reported. It was pointed out that some of the thorium oxide may have been dissolved by the hydrofluoric acid, thereby giving the low result.

An improved method of analysis was developed by MIT. This procedure yielded values of 1053, 1058 and 1072 ppm for the chips. The average of these values is reported in Section II. The new procedure involves complete dissolution with HCl and a trace of HF, followed by the addition of boric acid. The solution is filtered with paper pulp, ignited, and the thorium oxide residue weighed.

The Horizons Laboratory attempted a direct chlorination of the thorium metal at temperatures of about 900°C. The residue is ignited at 1000°C and weighed as thorium oxide. This procedure has not been fully validated, and the Horizons results are based on the insoluble residue method.

The vacuum fusion results which were reported for the solid sample were 930, 1030, and 1080 ppm. These values agree well with the insoluble residue results on the chips, indicating that the simpler insoluble residue test does appear to give a measure of the oxygen content for this grade material.

#### RARE EARTHS

Individual rare earth values are reported by ANL, BMI, and ORNL. ANL employed TTA extraction, and the copper spark method of spectrographic analysis. They generally had high detection limits and placed a factor of

2 reliability on their results. BMI and ORNL used the BMI method of cellulose column separation, followed by spectrographic analysis.

The sum of the averaged values of the individual rare earths is about 40 ppm as compared to a total rare earth value of 57 ppm obtained by NBL.

ORNL has done some work with the activation analysis for rare earths; however, no results are given for this program.

#### SILICON

The only colorimetric value reported is MIT's result of 46 ppm using ammonium tartrate.

In the spectrographic analysis, 2 laboratories reported silicon values of 25 and 10 ppm respectively. At 2 other laboratories, silicon was indicated as less than 50 ppm.

#### TIN

Three spectrographic analyses for tin gave a value of less than or about 2 ppm. A single result of 7 ppm was determined for one sample. The detection limit in this case was about 2 ppm.

#### TITANIUM

The Ames colorimetric determination with hydrogen peroxide as the oxidizing agent gave a value of 7.5 ppm, compared with ORNL's spectrographic value of 1.0 ppm. The 7.5 ppm value probably represents the detection limit for titanium according to the Ames procedure.

URANIUM

Four laboratories reported uranium values by the fluorometric method. The results appear consistent and ranged from 1.8 to 2.4 ppm. In all fluorometric determinations the uranium and thorium were separated prior to analysis because of the quenching effect of thorium on uranium fluorescence. This is indicated by the following KAPL data:

<u>g Th/fusion of 80 mg NaF</u>	<u>% Quenching</u>
6090	88
3050	85
1520	82
760	75
380	68
190	60
95	48
48	34
21	25
18	10

One laboratory performed a colorimetric analysis for uranium and obtained a value of 10 ppm. It was expected that this value is high because of errors caused by a time lag in making the colorimetric readings.

ZINC

A colorimetric value of 3 ppm was reported by BMI using dithizone. Polarographic determinations were made at Ames and ORNL. Ames questioned the reliability of their result because of the infrequent use of the polarograph at their laboratory. The ORNL polarographic value agreed with the colorimetric result.

Spectrographic results were found, in most cases, to be at the detection limits. The NBL value of 24 ppm is open to question because, in 5 additional samples, zinc was not detected.

The KAPL value of 87 is the average of 63, 102, and 98 ppm. The 63 ppm value was obtained on the concentrated sample where the detection limit is given as 5 ppm. The other values were obtained on dilute samples where the detection limit is ten times higher.

#### ZIRCONIUM

Spectrographic values for zirconium range from about 300-500 ppm. It was pointed out that since zirconium usually contains from 2-3% hafnium, it may be expected that the thorium contains about 10 ppm hafnium on the basis of these zirconium results.

## SECTION II. SAMPLE PREPARATION AND ANALYTICAL RESULTS

### PREPARATION OF THORIUM SAMPLES

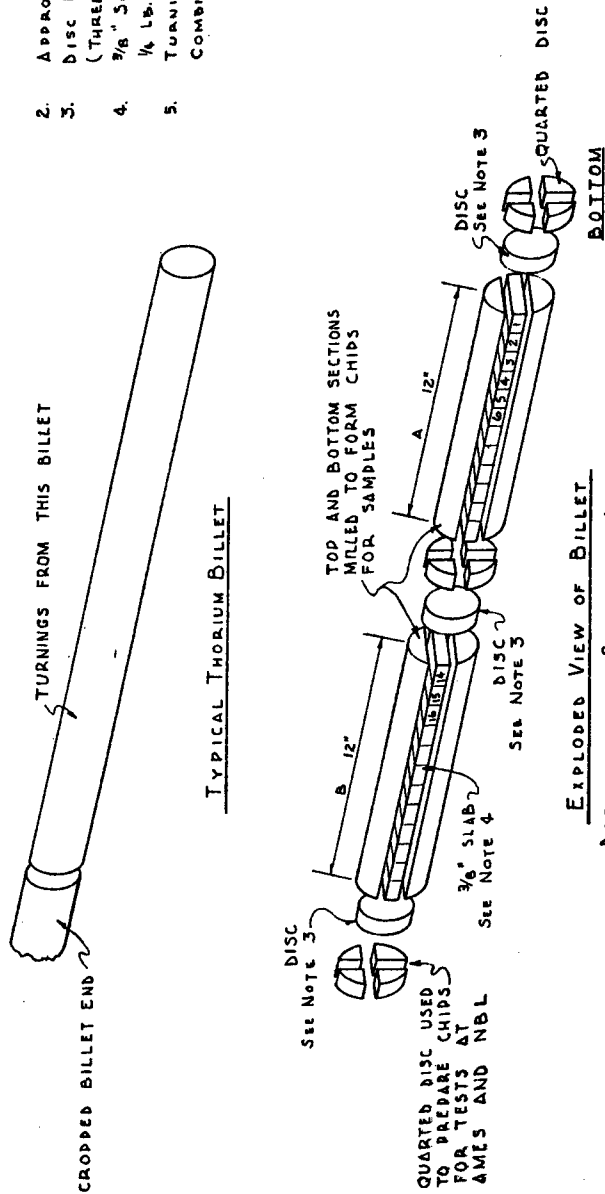
The accompanying diagram (Figure 1) indicates how the Ames thorium billet was divided to provide analytical samples for the participating laboratories. This billet, A-520, is representative of the material formerly produced in quantity at the Ames Laboratory.

In preparing this billet for use, six discs were cut from the billet, two from the top, two from the bottom, and two from the center. The two outermost discs and one of those removed from the center were then quartered. Two of the quarters in each disc were analyzed by the Ames and New Brunswick Laboratories to determine if the billet were typical of Ames production and therefore suitable for the analytical program. The remaining discs were converted by Ames to specimens for use in the danger coefficient test, as described in Section V.

The two cylindrical portions of the billet remaining after removal of the discs were then milled, leaving two  $3/8$ " solid slabs. The chips formed by the milling operation were passed over by a magnetic separator to remove any iron which may have been introduced in the milling process. The chips were then mixed in a stainless steel barrel mixer to obtain sample material as homogeneous in nature as possible. The  $3/8$ " thick center slabs were cut into one-quarter pound samples which were distributed, along with a portion of the chips, to the various participants in the program. Chipping was done under an inert atmosphere. Some of the chips and solid slabs are being retained for those interested in developing analytical procedures or checking the methods described in this report.

## NOTES:

1. APPROXIMATE BILLET DIMENSIONS:  
LENGTH: 26"  
DIAMETER: 3"
2. APPROXIMATE BILLET WEIGHT: 80 LBS.
3. DISC USED FOR DAMAGE COEFFICIENT TESTS  
(THREE DISCS IN ALL) ~ 1.5 LBS EACH
4. 3/8" SOLID CENTER SLAB (CUT INTO  
1/4 LB. SAMPLES FOR ANALYSIS)
5. TURNINGS FROM BILLETS A AND B  
COMBINED FOR STANDARD SAMPLE



NOT TO SCALE

Figure 1

## ANALYTICAL RESULTS

### Presentation of the Data

The following pages present the analytical results as contributed by the Thorium Analytical Program participants. An attempt is made to include as much information as possible on the data sheets, while largely leaving the interpretation and evaluation of individual results to the reader. As an aid towards this end, the data has been placed on a consistent basis whenever possible.

Those elements for which analyses were conducted are listed alphabetically, on p. 28, together with a designation of the analytical method employed. The majority of data was obtained on the thorium chips. Data reported on the solid bar were distinguished by the symbol(s) printed after the method of analysis. All other analyses were conducted on the sample of chips.

The data were obtained at the laboratories as indicated, with the exception of the National Lead Company chemical results, which were produced at the New Brunswick Laboratory using NLC personnel.

Each "data square" summarizes the available information for a particular method of analysis applied to a single impurity element by one of the program participants. Blank squares appear when no values were reported. Those containing data have part or all of the following information, reading down:

1. The average value for all samples.
  2. The average deviation of the reported data, calculated as the average of the differences between the reported average and the value for each sample.
- In some instances, a value for deviation is reported where the basis for its calculation is unknown. These values are distinguished by the symbol, (U), following the values.



3. The number of individual samples used to obtain the average, followed by the number of aliquots or portions for each sample.

Each data sheet also includes a column entitled "average". These values are determined in accordance with the following provisions:

1. In those cases where the data for an element and a particular method of analysis are reasonably consistent, an average value for the impurity is indicated, based upon the data presented and considering:

- a. the analytical method used;
- b. the number of samples analyzed;
- c. the possible sources of contamination;
- d. the standards employed.

Admittedly, the average value then is a somewhat arbitrary number. It is included only as an indication of the amount of impurity present, and is convenient for use in summarizing the results. The average value should not be construed as representing the absolute value of impurity concentration.

2. In certain cases the data is inconsistent or is quantitatively insufficient as compared to those cases under (1) above. It is desirable, nevertheless, to present some idea of the impurity value, although its determination may be fairly arbitrary. An attempt is made to note a representative or approximate value in these cases, while considering the same factors as in (1) above. These values are enclosed in parentheses.

3. "Average" values are omitted for analyses of the solid sample, with the exception of values of hydrogen, oxygen and nitrogen. This is done since in most instances very little data are available for the solid sample, and because there is a likelihood of segregation in the solid sample not probable for the chips. Since the chips may be air

contaminated, the solid sample average values for nitrogen and oxygen are included for comparison and possible evaluation of the effect of the contamination. The solid sample average value for hydrogen is included to supplement the one hydrogen analysis on the chips.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
ALUMINUM	Fluorometric						33 + 0 - 2-				(33)
	Spectrographic	10 +2 -2 3-	20*	6		22 +4 -1-3		50**	210*** - 7-1	5 +0 1-2 1-1	10
	Spectrographic(s)								210 - 6-1		

\* Controlled by residual impurity in matrix material

\*\* Attributed to Al contamination.

\*\*\* Means about 10 ppm.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HCR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
ANTIMONY	Spectrographic			<5							(<5)
BARIUM	Spectrographic			<5							(<5)
BERYLLIUM	Spectrographic	77 +2 - 3-	90	68						61 +2 - 1-2	70
BISMUTH	Spectrographic					2 - 1-1					(2)

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
BORON	Colorimetric		<0.2					0.4	0.4		
								+0.0	+0.1		0.4
								2-	6-1		
	Colorimetric(s)								0.4		
									-		
									1-1		
	Spectrographic	0.34*	0.1	0.2				1	a0.4	a1	0.3
		+0.02							-	-	
		6-							7-1	3-2	
	Spectrographic(s)								a0.6		
									-		
									6-1		

\*Av. of values for 3 air oxidized & 3 "oxide by dissolution" samples.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES-PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
CADMIUM	Colorimetric			< 0.2							(< 0.2)
	Spectrographic	0.16	< 0.5	< 0.1				< 0.25	± 0.1	< 1	0.1
		± 0.01							-	-	
		3-							7-1	2-1	
	Spectrographic(s)								± 0.1		
									-		
									6-1		

ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM											
ELEMENT	METHOD OF ANALYSIS	AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
CALCIUM	Spectrographic	17	40*	5		14			al5	110**	15
		+1 3-				- 1-1			- 7-1	- 1-1	
CARBON	Spectrographic(s)								<10		
									-		
									6-1		
CARBON	Combustion	410	410	330*** 400****	577	120	417	365	360	380	390
		+10 3-1	+18 3-1		+44 3-1	+5 2-1	+9 3-1	+15 2-1	+20 4-3 1-2	+160 -1-2 1-1	
	Combustion(s)								360		
CERIUM	Spectrographic		40	21						24	25
										+4 1-2 1-1	

\*Factor of 2 reliability (20 ppm Ca residual in matrix material).

\*\*\*Glober ignition.

\*\*\*\*Induction ignition.

\*\*Reason for high value not determined.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
CHLORINE	Nephelometric		13 +6 15-				16 +6 4-				(15)
CHROMIUM	Colorimetric		11 +1 4-1	10							10
	Spectrographic		8	12		5 - 1-1			a8 - 1-1	12 +0 2-1	10
	Spectrographic(s)								a5 - 1-1		
COBALT	Spectrographic			<2							(<2)



ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
COPPER	Colorimetric		4						4		4
			+3 8-						+0 2-1		
	Spectrographic		5	6		5		2	1-5	4	4
						+1 1-3			+0.2 6-2 1-6	+0 1-2 1-1	
	Spectrographic(s)								1.5*		
									+0.3 4-2		
DYSPROSIUM	Spectrographic		<1								<1)
ERBIUM	Spectrographic		<1	<0.4							<0.4)

\*Omits data for 2 contaminated samples. The omitted values are 200 for the first and 6 & 13 for the second.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
EUROPIUM	Spectrographic		<0.3	<0.5							(<0.3)
GADOLINIUM	Spectrographic		1*	0.35							(0.35)
GERMANIUM	Spectrographic			<2							(<2)
HOLMIUM	Spectrographic		<5	<0.15							(<0.15)

\*Probably unreliable according to ANL.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
HYDROGEN	Vacuum Fusion					16* +16(u) -					(16)
	Vacuum Fusion(s)			4 +2 4-1		4* +3(u) -					(4)
INDIUM	Spectrographic			<5							(<5)

\*Uncorrected for recovery.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NBL	ORNL	AVERAGE
IRON	Colorimetric	57	66	50		61	50	66	72		60
		+3 -2 (U)	+1 -1 4-1			+1 -2 1-2	+1 -1 1-4	+2 -1 2-1	+2 -1 4-2 1-3		
	Colorimetric(s)					55 +1 -1 1-2					
	Spectrographic	48 +2 -3	70	55				50	52* +20 -5-2 1-6		55
	Spectrographic(s)								52 +11 -6-2		
LANTHANUM	Spectrographic		4	3.3						5	4
										+1 -2-2	

\*Omits data for 2 contaminated samples. The omitted values are 120 and 110.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
LEAD	Polarographic									12*	
										+3 - 1-2	
	Spectrographic		5	2		all**		<1	al		
						- 1-1			- 7-2		(5)
	Spectrographic(s)								al***		
									- 4-2		

\* Variation from spectrographic data not explained.

\*\* Detectability limit high.

\*\*\* Omits data for 2 contaminated samples. The omitted values are 23, 30; 13, 15.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
LITHIUM	Flame Photometer									<1 - 1-1	<1
	Spectrographic		<1	<1							<1
LUTECIUM	Spectrographic			<0.1							(<0.1)
MAGNESIUM	Spectrographic	<20 - 3-	<10	3		10 3 1-3		15	al5* - 6-1		(10)
	Spectrographic(s)								al8 - 6-1		

\*Omits a contaminated sample value of a200.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NBL	ORNL	AVERAGE
MANGANESE	Colorimetric	< 2	< 5	1.9					2		2
		-	-						+0		
			2-1						3-2 2-1		
	Spectrographic	< 20	2	1.2		1.2		< 5	all	1.4	
		-				-			-	+0.3	2
		3-				1-1			7-1	2-1	
	Spectrographic(s)								all		
									-		
									6-1		
MOLYBDENUM	Colorimetric			2							(2)
	Spectrographic		< 10	< 2							(< 2)

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
NEODYMIUM	Spectrographic		9	4-5						6	6
										+2 2-2	
NICKEL	Colorimetric	26	29	26						28	27
		+2(V)	+2							-	
			4-1							1-1	
	Spectrographic		20	35		26		>50	52	24	26
						+6			+8	+2	
						1-3			6-2 1-6	3-2	
	Spectrographic(s)								26		
									+3		
									6-2		



ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
NITROGEN	Kjeldahl	74	55	60	20*	51	61	64	60	110**	60
		+6(U)	+3		+1	+2	+2	+1	+4	-	
		12-1	3-1		2-3	4-1	5-1	2-1	5-5	1-1	
	Kjeldahl(s)				20*						
					+3						
					1-3						
	Vacuum Fusion					22***					
						+9(U)					
	Vacuum Fusion(s)			25		12***				10	(16)
				+5		+9(U)				+0	
				2-1						2-1	

\* Data deemed questionable by HOR.

\*\* Reason for variation not determined.

\*\*\*Low values, uncorrected for recovery.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
OXYGEN	Insoluble Residue	1221		1120	1090		1061	1110	1118		1100
		+33 (U)		+7	+7		+7	+20	+1		
		201		3-1	3-1		3-1	2-1	1-2 1-1		
	Insoluble Residue(s)				1333				989		
					+125				+5		
					3-1				1-2		
	Vacuum Fusion(s)		1030	1080		1760*				930	(1100)
			+80	+10		+180 (U)				+20	
			5-1	2-1		-				2-1	
PRASEODYMIUM	Spectrographic		<5	<1.2							<1.2

\*An average value for chips and solids

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NBL	ORNL	AVERAGE
SAMARIUM	Spectrographic		< 2	< 0.5							(0.5)
SILICON	Colorimetric						46 47 1-3				(46)
	Spectrographic	< 50 - 3-	< 50	25				10			< 50
SILVER	Spectrographic								0.2 - 7-1		(0.2)
	Spectrographic(s)								0.2 - 6-1		

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
SODIUM	Spectrographic								all - 7-1		(15)
	Spectrographic(s)								all - 6-1		
STRONTIUM	Spectrographic			<1							(<1)
THALLIUM	Spectrographic			<1							(<1)
THULIUM	Spectrographic		<1	<0.15							(<0.15)



ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
URANIUM	Colorimetric	10*									
		$\pm 3$ (U)									
			2.4 $\pm 0.2$ 3-	2.0 $\pm 0.2$ (U)		1.8 $\pm 0.6$ 1-3				1.9 - 1-1	2
VANADIUM	Spectrographic										
YTTERBIUM	Spectrographic										

\*Ames indicates this value is high.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	EMI	HOR	KAPL	MIT	NLC	NEL	ORNL	AVERAGE
YTTRIUM	Spectrographic		0.4	0.21							(0.3)
ZINC	Colorimetric			3							(3)
	Polarographic	6.5								2.6 +0.3 - 1-2	(4)
	Spectrographic	<20	<20	<20		87* +20 - 1-3		<5	24** - 2-2		<20
	Spectrographic(s)								13*** - 2-2		

\* Value Doubtful, partly because of detection limit.

\*\* In 5 additional samples zinc was not detected.

\*\*\*Omits data for a contaminated sample (280, 330 ppm), and 3 samples in which zinc was not detected.

ELEMENT	METHOD OF ANALYSIS	ANALYTICAL RESULTS - THORIUM METAL SAMPLES - PPM									
		AMES	ANL	BMI	HOR	KAPL	MIT	NLC	NBL	ORNL	AVERAGE
ZIRCONIUM	Spectrographic	315 + 7 3-	400						a500		(400)
	Spectrographic(s)								a500		
TOTAL RARE EARTHS	Separations								57 - 1-1		(57)
	Separations (s)								75 - 1-1		



## SECTION III. CHEMICAL PROCEDURES

ALUMINUMAMES

The Ames procedure was not employed in this program. It has, however, yielded results which agree well with the Ames spectrographic data, and is therefore included in this report.

A 4 g thorium sample is dissolved in a 100 ml beaker by warming with 50 ml 1:1  $\text{HNO}_3$  and 2 ml of a 0.015 %  $\text{H}_2\text{SiF}_6$  solution. The excess  $\text{HNO}_3$  is evaporated and the solution diluted to volume in a 100 ml volumetric flask. To a 25 ml aliquot one ml of 10% hydroxylammonium chloride solution and 20 ml of 0.1% 1,10-phenanthroline solution are added. The tris (1,10-phenanthroline)iron(II) ion forms after a few min. The solution is buffered with 100 ml of acetate solution (300 g ammonium acetate : 300 ml glacial acetic acid and water to make one liter of solution). The pH is adjusted to 4.80.

The solution is transferred to a 250 ml separatory funnel and exactly 20 ml of 1% 8-quinolinol solution in chloroform is added. The solution is shaken once, any gas released, followed by 3 min of shaking.

After the phases separate, the lower layer is transferred to another separatory funnel containing 25 ml of the acetate solution, 20 ml of 1,10 phenanthroline solution, one ml of hydroxylammonium chloride solution, and 50 ml  $\text{H}_2\text{O}$ . The extraction is repeated.

Zinc, copper, cobalt, and nickel interferences are removed by transferring the chloroform-8-quinolinol extract to another separatory funnel containing 100 ml alkaline cyanide solution (20 g KCN, 10 ml conc.  $\text{NH}_4\text{OH}$ , and 40 g  $\text{NH}_4\text{NO}_3$  per liter of aqueous solution. The

extraction is performed, and the chloroform layer drained into a glass stoppered flask containing 1-2 g of anhydrous  $\text{Na}_2\text{SO}_4$ . The flask is shaken and allowed to stand, unexposed to sunlight, for 15 min.

The absorbancy of tris (8-quinolinolo) aluminum (III) is measured in a Beckman, Model DU quartz spectrophotometer at 385  $\text{m}\mu$ . Matched 1-cm Corex cuvettes are used. A blank is run through the entire procedure.

A calibration curve is obtained by preparing a series of solutions containing varying known amounts of aluminum from 10 to 120  $\mu\text{g}$ . These solutions, made by dissolving very pure aluminum metal in reagent-grade sulfuric acid, are treated as was the aliquot above. The plot of absorbancy against  $\mu\text{g Al}/20\text{ ml}$  of chloroform-8-quinolinol solution conforms to Beer's law over the concentration range of 0-120  $\mu\text{g}$  of Al per 20 ml of chloroform-8-quinolinol solution.

#### MIT

A one gram sample is placed in a 280 ml platinum dish and treated with 25 ml of 1:1  $\text{HNO}_3$  containing 2 drops of 48% HF. Digestion is done just below boiling. After complete solution is obtained, 100 ml of water and 15 ml  $\text{HNO}_3$  are added. The solution is heated to incipient boiling and 20 ml 10% oxalic acid are added slowly, while stirring with a platinum rod. Digestion just below boiling follows for 1/2 hr. The cooled solution is transferred to a 200 ml volumetric flask, and water added to the mark. The solution is mixed and returned to the platinum dish.

After the crystalline precipitate settles, 20 ml of the clear solution is evaporated to dryness, and the oxalic acid eliminated by heating the residue on a sand bath under an infra-red lamp. A few

drops of  $\text{H}_2\text{SO}_4$  are added and, after heating to fumes, the residue is ignited over a Bunsen flame.

The residue is fused with one gram of fusion mixture (1 part  $\text{Na}_2\text{B}_4\text{O}_7$  to 4 parts  $\text{Na}_2\text{CO}_3$ ), and the melt dissolved in 20 ml hot water. Filtering is done through an S and S "blue" filter paper. The filtrate is collected in a 100 ml beaker containing 1.65 ml acetic acid.

The aluminum in this solution is determined by the fluorometric method described by Allan R. Eberle.

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A. R. Eberle. "Fluorometric Determination of Aluminum in Zirconium Metal and Zirconium Oxide," NYO-2013, issued Jan. 22, 1951.

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BORONANL

A one gram sample is decomposed in quartz flasks with an amount of hydrochloric acid calculated to convert the metal to thorium chloride. The sludge remaining after the acid treatment is partially neutralized by the addition of 0.2 g of calcium metal. Purified methanol is added and the distillation carried out until 80 ml is collected in a beaker containing 15 ml of 0.1N  $\text{Ca}(\text{OH})_2$  suspension. The alcoholic solution is transferred to porcelain dishes and evaporated to dryness. The color developed by oxalic acid-turmeric at  $55^\circ\text{C}$  is extracted with 70% ethanol. The extract is diluted to 10 ml, centrifuged and the transmittance measured at 540 m $\mu$  using 1 cm cells.

NLC

A 0.5 g sample is dissolved in dilute nitric acid. Hydrochloric acid is added and the sample refluxed for one hr. The solution is then neutralized with sodium hydroxide and subsequently made slightly acid with hydrochloric acid. Calcium chloride salt and methyl alcohol are added, and the methyl borate is steam distilled into a dilute sodium hydroxide solution. The boron content of the distillate is determined colorimetrically using turmeric as the chromogenic reagent. Optical density is read at 540 m $\mu$ , and the boron concentration determined by comparison with standard curves.

NBL

A 0.5 g thorium sample is placed in a 60 ml quartz distilling flask and 2.5 ml 1:4  $\text{HNO}_3$  are added. The flask is connected to a quartz reflux condenser (36 in. long & 7 mm diam.) by means of a two-hole rubber stopper containing a quartz reagent tube. Five ml of water and 6 ml of  $\text{HCl}$  are added dropwise through the tube. When the reaction has subsided, 4 drops of 1%  $\text{HF}$  are added through the tube and the mixture refluxed gently until the sample dissolves.

After the solution has cooled, the flask is removed, and the excess acid neutralized by the dropwise addition of a saturated ammonia solution. The sample is kept cold and mixed slowly to avoid loss of fumes, and to redissolve the precipitate which is formed. When no more precipitate dissolves after swirling and standing for ten min, hydrochloric acid is added dropwise while swirling the flask, to just dissolve the remaining precipitate and 4 drops in excess. (The solution must be sufficiently acid to prevent plugging of the tube before distillation is complete.) The neutralization takes approximately 5 ml of ammonia.

After all fumes have settled, 25 ml 10%  $\text{CaCl}_2$  in methanol are added; and the flask is connected to a still which has been provided with a 200 ml receiving dish (well-glazed Coors #4A porcelain) and a flask containing 25 ml of methanol and a pellet or two of sodium hydroxide. The receiving dish is supported in an enclosed cold water bath which consists of a 6 in. crystallizing dish with a plastic (Pittsburgh Plate Glass CR-39) cover, and is protected from the heat of the burners by a transite shield. The condenser tube passes through a hole in the center of the cover almost to the bottom of the receiving dish (Figure 2).

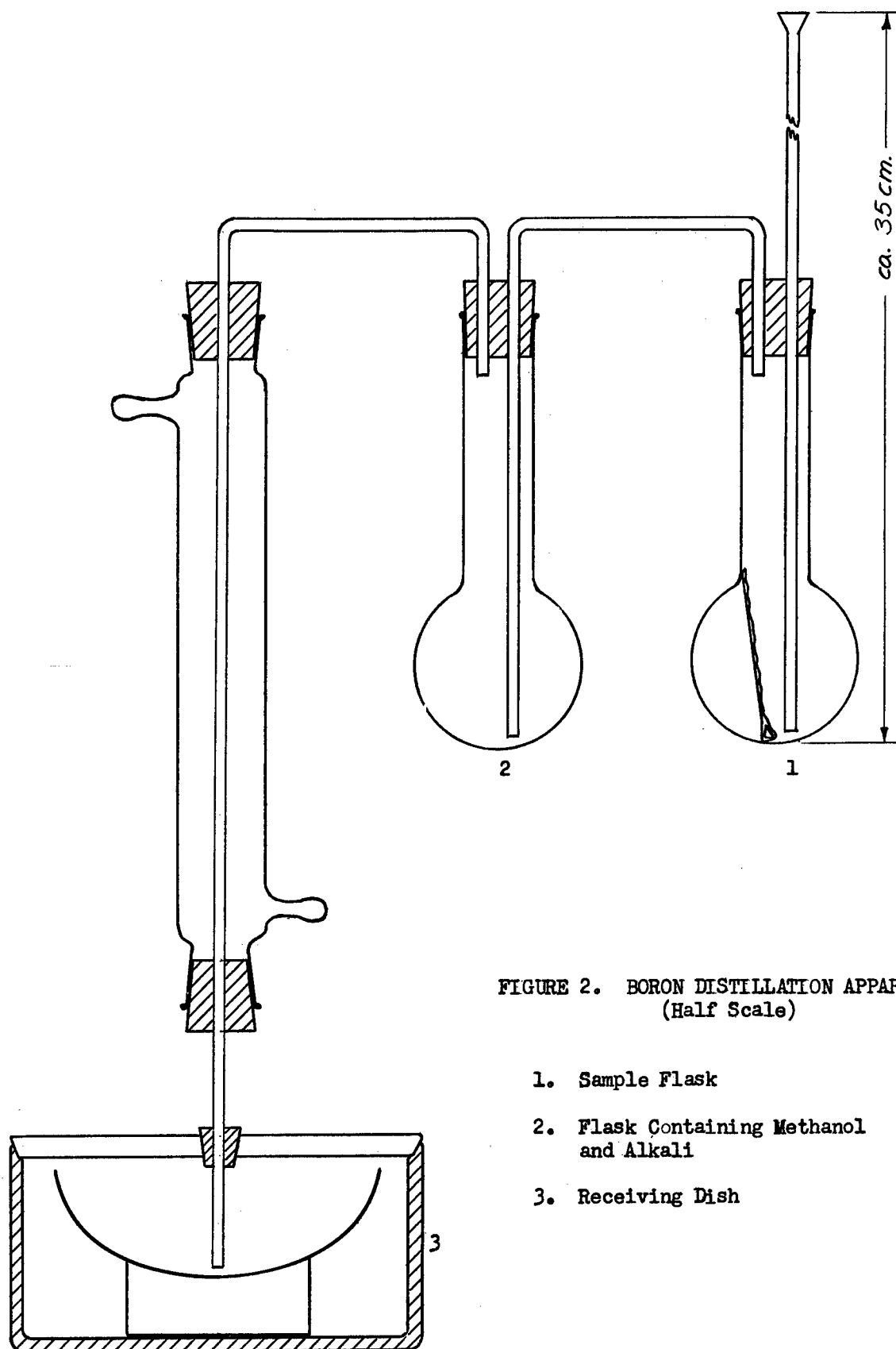


FIGURE 2. BORON DISTILLATION APPARATUS  
(Half Scale)

1. Sample Flask
2. Flask Containing Methanol  
and Alkali
3. Receiving Dish

Immediately after connection of the sample flask to the still, 5 ml of 0.1 N lime are added to the receiving dish. Then each flask is immersed in a beaker of hot water. Beaker A is kept at 76-78°C and beaker B at 80-82°C. As the alcohol in flask B distills over, successive 25 ml portions are added until a total of 125 ml has been added to flask B. The volume of solution in flask A is kept ca. 40 ml by controlling the temperature differences between the two beakers. After the alcohol has been distilled from B, heating is stopped, the stoppers in the flask are loosened and the end of the condenser tube is washed with 10 ml H<sub>2</sub>O. Immediately, an extra 5 ml of lime is added to the distillate and the solution evaporated to dryness on the steam bath.

The dry sample is ready for colorimetric analysis (It may be stored, if necessary, in a desiccator containing a small dish of sodium hydroxide pellets and sealed with vaseline.) The sample is cooled to room temperature and 2 ml of dilute oxalic-hydrochloric acid reagent are added. The dish is manipulated so as to bring the reagent into contact with all the lime. Then 2 ml of 1% turmeric extract are added and the dish twirled until all reagents are mixed thoroughly. Each of these reagents is added rapidly from a coarse tipped pipette. The dish is placed in a water bath containing enough water to nearly or just float the dish, and which is kept at 55 ± 1°C, until the sample is just dry and then for 30 or 45 min longer. The dish is removed and cooled. With the acid of a rubber tipped stirring rod, the precipitate is extracted with 20-25 ml of 90% ethanol added in about 5 ml portions.

The extracts are decanted into a 25 ml graduate, diluted to 25 ml with 95% ethanol (which was stored in boron-free glass), mixed and

filtered through double dry #1 Whatman filter paper. The transmittancy of the solution is determined using as a reference a blank obtained by carrying 5 ml of lime throughout the above procedure, beginning with evaporation on the steam bath. Known amounts of boric acid (0.5 - 1.5  $\mu$ g of boron) plus 5 ml of 0.1 N lime each are carried through the color development with each set of samples. Transmittancies are measured with a Beckman spectrophotometer at 540 m $\mu$ . The boron content of the test solution is obtained from the transmittancy-concentration curve and then is corrected for a "reagent" blank which is run through all steps of the procedure and which should be about 0.1  $\mu$ g of boron. (This blank is due mainly to rubber stoppers. Several distillations may be required on new stills to achieve a relatively constant blank.)

A correction is also made for the average loss in the solution, neutralization, and distillation steps. This averages to about 10% and is determined by analyzing samples both alone and with added amounts of boron.

Great care must be taken to avoid contamination from glassware, etc. Fused quartz must be used throughout for carryout reactions and storing reagents unless otherwise stated.

#### Reagents

The acids and sodium hydroxide are all C.P. grade. The saturated ammonia solution is prepared in quartz from tank ammonia, and the reagent absolute (or synthetic) methanol is purified by distillation from potassium or sodium hydroxide in quartz apparatus.

Calcium Chloride, 10% in Methanol. About 35-70 g of distilled calcium is cleaned by washing with distilled water and scraping off the oxide



formed. The clean metal is weighed and placed in a large silica dish which is placed in a pan of ice and water. One hundred to 300 ml of  $H_2O$  are added, then 4.4 ml  $HCl/g$  Ca are added rather rapidly, using the bath to control the reaction rate. After the calcium has reacted, methyl red and a quartz boiling tube are added, and hydrochloric acid is added to give an acid reaction that is permanent even at the boiling point. The solution is boiled down to a volume of 3.0 - 3.8 ml/g of Ca. The solution is cooled, and diluted with purified methanol to 28 ml of solution per g of calcium used.

Calcium hydroxide, 0.1 N suspension. A piece of distilled calcium, cleaned as above, of about 0.80 g is dropped into a 500 ml quartz flask containing 0.5 ml of  $H_2O$  for each mg of calcium. After the metal has decomposed, the flask is closed with a rubber stopper containing a quartz tube which is used for transferring approximately 5 ml portions of the suspension. (The suspension is mixed before each portion is removed.) The top of the tube is covered with a small rubber bulb when not in use.

Dilute Oxalic-Hydrochloric Acid Solution. To 40 g of  $(COOH)_2 \cdot H_2O$  in a 500 ml quartz flask is added 270 ml of water and 160 ml of 95% ethanol. After the oxalic acid dissolves, 50 ml of  $HCl$  are added and mixed. This solution may be used for several months.

Turmeric, 1% Extract. Prepared by stirring 1 g of turmeric in 100 ml of boron free, 95% ethanol for 4 hours, and filtering through #42 Whatman filter paper from which boron has been removed previously by washing with ethanol (or by washing with dilute hydrochloric acid and then with water until free of acid in which case the paper is dried before use). The extract is prepared and stored (in the dark) in boron-free flasks.

CADMIUMBMI

A sample containing 5 to 40  $\mu\text{g}$  of cadmium is placed in a 250 ml beaker; 15 ml  $\text{HNO}_3$  and 25 ml  $\text{H}_2\text{O}$  are added. The addition of a few drops of  $\text{H}_2\text{SiF}_6$  followed by gentle warming effect solution of the metal. The excess nitric acid is removed by boiling until salts begin to separate from the solution. After the sample is cooled, 20 ml  $\text{H}_2\text{O}$  are added, and the thorium is complexed with sufficient 40% (w/v) ammonium citrate. (10 g Th: 125 ml citrate). The pH is adjusted with 10% NaOH solution to about 9.0, and the extraction performed with successive 5 to 10 ml portions of dithizone (20 mg per liter of  $\text{CHCl}_3$ ). When the dithizone solution remains unchanged green, the extraction is considered complete.

The chloroform extracts are washed with two portions of distilled water, and the water layer discarded. Washing is repeated with the portions of 0.05 N  $\text{H}_2\text{SO}_4$ . The combined acid extracts are washed with 10 ml  $\text{CHCl}_3$ , and the chloroform discarded. To the acid extract, 10 ml of 10% NaOH are added, followed by re-extraction with dithizone until no more color is removed. The extracts are diluted to 50 ml, filtered through a dry paper, and read in a 1 cm cell at 520  $\text{m}\mu$ . Chloroform is used as a reference. A blank is carried through all steps of the procedure.

## CARBON

### AMES

Carbon is determined using the Fisher Induction Carbon Apparatus. This apparatus produces an alternating electric field of 18 megacycles frequency causing metallic samples to heat to about 3000°C in 20 sec. The equipment contains a magnesium perchlorate drying tower to remove sulfur containing gases and water prior to the absorption of the carbon dioxide in caroxite or ascarite. The unit also contains a flow meter and a platinum oxidizer to convert any carbon monoxide to the dioxide. A resistance furnace capable of maintaining 800°C and containing a silica tube packed with copper oxide is used as a preheater.

For optimum combustion with the induction apparatus, the thorium sample is ground to minus 20 mesh in a Wiley mill under a helium atmosphere.

A sample weighing 2.73 g is placed in a ceramic boat containing a grooved bed of minus 100 mesh zirconia. The boat is placed in a ceramic sleeve and the sleeve is positioned in the reaction chamber. Ten minutes are allowed for warm-up of the apparatus. Using a modified timing system, a 20 sec preheat period, 200 sec combustion period, and 260 sec sweeping period are provided.

A blank determination is made using the boat, bedding material, and ceramic sleeve, and running for 8 min. The system is saturated with carbon dioxide by ignition of a thorium sample prior to the blank determination. The weight change of the Nesbitt absorption bulb should be less than 0.2 mg. If the weight change is greater than this amount

but is consistent, the blank may be used as a correction factor.

#### ANL

A 1 to 2 g sample of metal turnings on a bed of 60 mesh alundum in an alundum boat is ignited in oxygen at about 1200°C within a quartz combustion tube. Prepurification of the oxygen is accomplished by bubbling the gas through sulfuric acid, hot copper oxide (~700°C), ascarite and magnesium perchlorate. The exit gases are passed through hot copper oxide, silver wool, magnesium perchlorate, and the carbon dioxide absorbed in ascarite and weighed.

#### BMI

A sample weighing 0.5 to 1.0 g in the form of metal powder or small chips is ether washed, dried, and placed in a Combax combustion boat. About 0.5 g of electrolytic iron and 2 strips of copper (Leco or equivalent) are added. The boat is placed in the hot zone (2600°F or 1430°C) of a standard Globar-type furnace, and preheated for 3½ min. Oxygen is introduced at the rate of one liter per min, and continued until the jacketed gas burette is filled. Prepurification is done with sulfuric acid, ascarite, and drierite; the purifier consists of manganese dioxide. The carbon dioxide is absorbed in a caustic pipette, and a relative carbon value determined. Adjustments are made for sample weight, temperature, and barometric pressure. A blank is deducted for carbon present in the copper-iron flux.

This procedure is used when the carbon content is greater than 0.01%. For carbon less than this value, a Leco low-carbon determinator (Induction-furnace conductometric measurement) is employed.

HOR

Carbon determinations are done using a Leco semi-automatic carbon determinator containing a Burrell Globar tube furnace.

A 0.25 g sample is used for carbon contents up to 1.5% and a one g sample is used for carbon up to 6%. The sample is placed in a ceramic boat, covered, and placed in the cold zone of the furnace. The use of an accelerator is optional. The furnace is preheated to about 2200°F (1200°C), and the sample is pushed into the hot zone. After heating for 50-60 sec, the oxygen is introduced until a carbon burette is filled with the combustion gases. Absorption is done in potassium hydroxide solution, and the burette reading adjusted for temperature and pressure corrections.

KAPL

A high frequency induction heating method is employed using low carbon steel as a flux. The sample is analyzed "as received" and the combustion temperature is in the range of 2500-3000°C.

MIT

A Burrell combustion furnace is used. About a one or two gram sample of metal chips is burned in purified oxygen at 1300°C. The carbon dioxide is absorbed in ascarite and weighed.

NLC

A 2 g sample is ignited at 1300°C in a stream of purified oxygen using a Burrell combustion furnace. The carbon dioxide is passed through a manganese dioxide purification tower and absorbed in a standard solution

of barium hydroxide. The solution is titrated with 0.1 N HCl and the carbon content calculated.

#### NBL

The carbon content in a 2 g sample of chips is found using a Burrell combustion and associated apparatus shown in Figure 3. The furnace is preheated to 1300°C with oxygen passing through, and the combustion apparatus checked for leaks. The titration apparatus is attached. The buret is filled with standardized 0.05 N HCl, and to the absorption tube is added 10.00 ml of 0.04-0.05 N Ba(OH)<sub>2</sub> with 4-5 drops of thymolphthalein indicator (1 g solid in 100 ml C<sub>2</sub>H<sub>5</sub>OH).

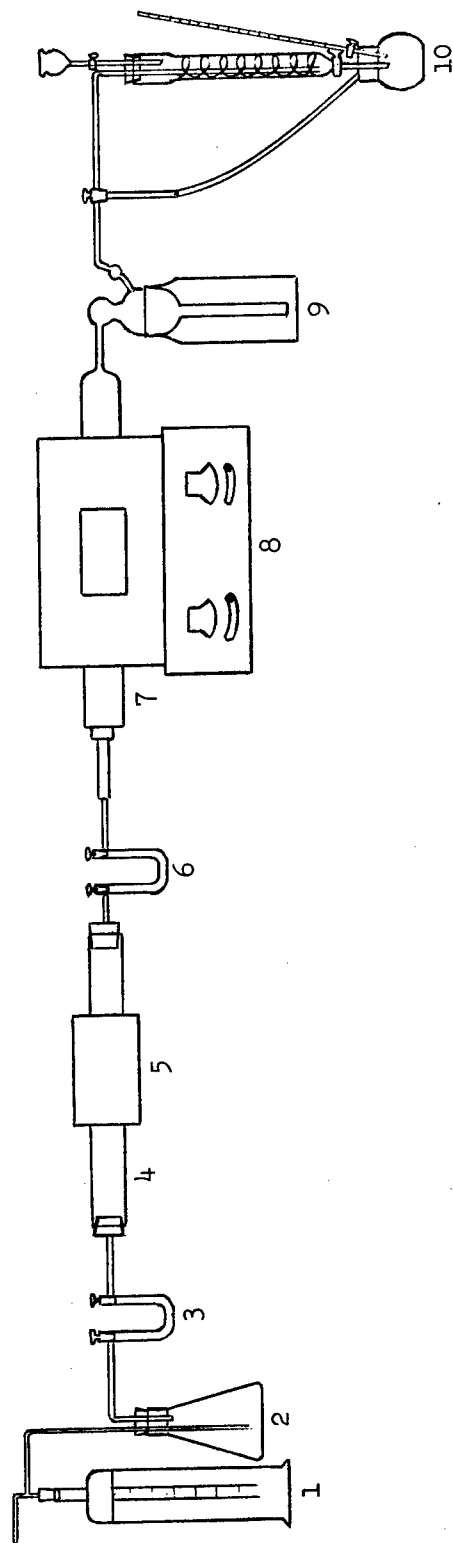
The sample is placed in a Zircofrax boat, the boat covered, and inserted into the combustion tube. The oxygen is quickly turned on and allowed to flow through the train for 25 min. The barium hydroxide is run into the receiving flask and the absorption tube washed twice with boiled distilled water. Titration is done slowly, with continuous swirling, to the end point.

Blanks are made before any samples are analyzed, and the performance of the train checked with a standard stainless steel sample.

#### ORNL

A sample of chips is analyzed directly by the combustion method. Oxidation temperature is about 1300°C.

FIGURE 3 NBL CARBON APPARATUS



1. Pressure Regulator  
(Pressure maintained at 4" Hg.)
2. Sulfuric Acid Overflow Trap
3. Drierite Guard Tube
4. Vycor Combustion Tube (filled with copper oxide and heated to 600-650°C)
5. Preheater
6. U-tube (half filled with Ascarite; the balance contains  $Mg(ClO_4)_2$  plus a little indicating Drierite.)
7. McDaniels or Zircofrax Combustion Tube (1-1/4" I.D. with tapered end. Inlet end closed with a rubber stopper having a steel inlet tube with steel and asbestos baffles. This end is always water cooled.)
8. Burrell High Temperature Furnace
9. Sulfur Trap (gas washing bottle 2/3 filled with conc.  $H_2SO_4$  saturated with chromic acid.)
10. Titration Apparatus (A three-way stopcock leads from combustion tube to a Zackerl-Krainick Absorption buret which in turn drains into the receiving flask. A 10 ml buret also leads into the flask.)

CHLORINEANL

A one gram sample is dissolved in 6 N  $\text{HNO}_3$  and enough ammonium fluoride to make the solution 0.01 to 0.03M in the fluoride ion. The solution is filtered, washed, and diluted to a 50 ml volume. The chloride is precipitated with 0.01 N  $\text{AgNO}_3$ , digested at a constant temperature of  $40^\circ\text{C}$  for 1/2 hour, and measured on a nephelometer. From a curve, previously plotted from standards that are carried through the above procedure, the concentration of chlorine is determined. The dissolving is done in pyrex.

MIT

The chlorine is determined by a nephelometric method after solution of about one gram of the metal in dilute nitric acid containing two drops of 48% HF. Dissolution is done in platinum ware.



CHROMIUMANL

For the analysis of chromium, iron, nickel and manganese, a sample of chips weighing about 6 g is dissolved in a platinum beaker using ca. 6 N  $\text{HNO}_3$  and a trace of hydrofluorine. After dissolution, the solution is evaporated just to dryness, and the thorium nitrate salts dissolved in water, transferred to a 200 ml volumetric flask, and diluted to volume.

A 5 ml aliquot is diluted to 25 ml in a 50 ml beaker. Five drops of sulfuric acid are added. The solution is heated to near boiling and 5 drops 1 %  $\text{AgNO}_3$  + 4 ml  $\sim 0.002\text{M}$   $(\text{NH}_4)_2\text{S}_2\text{O}_8$  are added. Near boiling temperature is maintained for 20-30 min. After transfer to a 25 ml volumetric flask, the solution is cooled in an ice bath, and the color developed by the addition of 1 ml 0.4% diphenylcarbazide in ethanol. The solution is diluted to volume and read at 540  $\text{m}\mu$  against a reagent blank. The amount of chromium present is read from a previously prepared transmittance-concentration curve.

BMI

A sample containing from 0.03 to 0.30 mg Cr is dissolved in 5 ml  $\text{HNO}_3$  and 5-10 drops 0.05 M HF using a 250 ml beaker. After warming to dissolve traces of the oxide, 5 ml  $\text{H}_3\text{PO}_4$  and 50 ml  $\text{H}_2\text{O}$  are added, followed by boiling to remove the oxides of nitrogen. Two drops of saturated potassium permanganate solution are added and the solution boiled for 5 min. Conc. HCl is added dropwise until the permanganate is decomposed and a clear solution is obtained. The solution is boiled 30 sec, cooled to room temperature in an ice bath, and transferred to a 250 ml volumetric flask containing 150 ml  $\text{H}_2\text{O}$ . Two ml 0.5% diphenylcarbazide solution

(0.5 g diphenylcarbazine in 10 ml glacial acetic acid, dilute to 100 ml with ethanol) are added, the solution diluted to mark, mixed, and read within 15 min at 550 m $\mu$  in a 1 cm cell. Water is used as a reference.

COPPERANL

A sample weighing about 10 g is dissolved by treating first with HCl and then  $\text{HNO}_3$  and a small amount of  $\text{NH}_4\text{F}$ . Excess acid is removed by heating on a steam bath. The solution is diluted to 200 ml and a 10 ml aliquot taken for analysis. To the aliquot are added 4 ml of 50% citric acid, 5 ml of 5% sodium pyrophosphate, one ml of 1% dimethylglyoxime, and 8 ml of ammonium hydroxide. The pH should be greater than 9. One ml of 2% sodium diethyldithiocarbamate is then added, and the solution extracted three times with 5 ml portions of isomylalcohol. The alcohol extract is diluted to 25 ml, and the color measured spectrophotometrically in 5 cm cells at 440 m $\mu$ .

ORNL

The colorimetric method with diethyldithiocarbamate is employed. Measurements are made on a Beckman DU spectrophotometer.

HYDROGENBMI

The tin-fusion analysis is used for hydrogen. This analysis is carried out in a carbon-free tin bath at 1150°C (2102°F). One hundred grams of C.P. tin (for a 5 g sample) contained in a fused silica crucible are degassed at 1150°C until a satisfactory furnace blank is obtained. The sample is then dissolved in the tin bath. The evolved gases are collected for 20 min and analyzed by the fractional freezing method. Prior to analysis, each sample is filed and then degreased in warm acetone.

KAPL

Hydrogen is determined by a vacuum fusion analysis of both the thorium chips and the solid metal. Recovery factors are not determined.

## IRON

### AMES

A 3-5 g thorium sample is dissolved in a 250 ml beaker by the addition of 100 ml conc. HCl. After gas evolution subsides, 25 ml conc. HNO<sub>3</sub> are added and the solution heated to boiling on a hot plate. The remaining residue is dissolved with the aid of a few drops of dilute fluosilicic acid (2 drops 48% H<sub>2</sub>SiF<sub>6</sub>/ 50 ml H<sub>2</sub>O) followed by digestion. The solution is then evaporated to a 10 ml volume, transferred to a 100 ml volumetric flask and diluted to mark.

An aliquot sample containing about one gram of thorium is transferred to a 100 ml volumetric flask and the following additions are made: a) 1 ml 10% hydroxylammonium chloride, b) 10 ml 0.1% o-phenanthroline, and c) 25 ml 25% ammonium tartrate. The solution is diluted to about 75 ml and 1:1 NH<sub>4</sub>OH is added with mixing until the white flocculent precipitate dissolves. The pH should be about 5.

After dilution to volume, the solution is allowed to stand for one hour or more, and the transmittancy then determined using a Coleman spectrophotometer at 515 mμ. Distilled water is used as a blank.

The calibration curve is prepared by taking 2, 4, 6, 8, 10, 15, 20, 30, & 40 ml aliquots of a standard iron solution (pure iron in dil. H<sub>2</sub>SO<sub>4</sub>) containing 10 μg Fe/ml. Hydroxylammonium chloride, o-phenanthroline, and ammonium tartrate are added as above, the solutions diluted to about 75 ml, and the pH adjusted to 5 ± .5 as shown by Hydrion paper. Transmittancies are made at 515 mμ, and the percent transmittancy vs. μg Fe/ml plotted on semilog paper.

ANL

A 10 ml aliquot of the sample solution described under the chromium procedure is transferred to a 25 ml volumetric flask. Two ml 10% hydroxylamine hydrochloride are added and the solution heated to near boiling in a water bath. The solution is cooled slightly and additions of 1 ml 10% hydroxylamine hydrochloride and 1 ml 0.1% o-phenanthroline are made. Ammonium hydroxide is then added drop by drop until the thorium hydroxide precipitate forms. Acetic acid is added dropwise until the solution clears. The solution is diluted to volume and read at 505 m $\mu$  against a blank on the reagents carried through the procedure. The amount of iron present is obtained from a previously prepared transmittance-concentration curve.

EMI

A sample containing from 0.05-0.40 mg Fe is dissolved in a 250 ml beaker in 10 ml HNO<sub>3</sub> and 5-10 drops of 0.05 M HF. The solution is warmed until all traces of oxide are in solution. Ten ml of saturated boric acid are added followed by warming for 10-15 min. After cooling to room temperature, the solution is transferred to a 100 ml volumetric flask and 10 ml of 30% ammonium thiocyanate in water are added. The solution is diluted to mark, mixed, and read immediately in a 1 cm cell at 480 m $\mu$ . For a reference solution, a sample is used with all reagents added except the thiocyanate solution.

KAPL

One ml of 2 M thorium is analyzed colorimetrically with o-phenanthroline (of KAPL-572) using sodium acetate as a buffer at a pH of 2-4. A Klett Summerson colorimeter with a 4 cm cell is used with a 540 m filter.

MIT

A 5.00 g sample is dissolved with 25 ml 1:1 HCl containing 10 drops of 48% HF per 100 ml. The solution is boiled to dissolve any remaining residue, then cooled and transferred to a 100 ml volumetric flask. After dilution to the mark and mixing, aliquots containing 1 g of thorium are transferred to beakers. The volumes are adjusted to 40 ml by addition of water. Hydroquinone, o-phenanthroline, and ammonium citrate are added. Dropwise additions of ammonium hydroxide are made until a heavy precipitate is formed, then 1:4  $\text{NH}_4\text{OH}$  is added drop by drop with stirring to adjust the pH to 3.5. After standing 24 hours, the volume is adjusted to 100 ml and the optical density read at 513 m $\mu$ , using a Beckman spectrophotometer. The iron concentration is found by comparison with a standard curve.

NLC

A 2 g sample is dissolved with dilute nitric acid, evaporated to dryness and the residue dissolved in dilute hydrochloric acid. Reduction is done with hydroxylamine, and o-phenanthroline is used as the chromogenic reagent. After adjusting the pH, the optical density is read at 515 m $\mu$  and the iron concentration found by comparison with a standard curve.

NBL

About a 2 g sample of metal is placed in a 250 ml beaker. Thirty ml of 1:1 HCl are added, and the sample heated on a steam bath. When the initial reaction has ceased, a few drops of very dilute (1:100) HF are added and the digestion continued until the sample is completely dissolved. The solution is evaporated to dryness and the residue dissolved in dilute

hydrochloric acid. This solution is transferred into a 100 ml volumetric flask, diluted to volume with water, and mixed.

A 50 ml aliquot is transferred to a beaker and 3 ml of 0.1% o-phenanthroline and 5 ml of 10% hydroxylamine hydrochloride are added. The pH is adjusted between 3 and 3.5 using a Beckman pH meter. The sample is diluted to 100 ml in a graduate and mixed. A reagent blank is run through the procedure with the samples.

The transmittancy of the solution is measured against the blank in a Beckman spectrophotometer at 515 m $\mu$  in 2 cm cells. A transmittancy-concentration curve is prepared by using the above procedure and solutions containing 0, 50, 100, 150, & 200 g Fe. Results are plotted on semi-log paper.

The standard iron solution is prepared by dissolving 7.020 g  $\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$  in 100 ml  $\text{H}_2\text{O}$ , adding 10 ml 1:1  $\text{H}_2\text{SO}_4$ , and diluting to one liter. This solution contains 1 mg Fe/ml.



LITHIUMORNL

The solution remaining after the extraction of thorium with TBP is converted to a hydrochloric acid solution and run through the flame photometer.

MANGANESEAMES

Five one gram samples of thorium are weighed into 150 ml beakers and treated with 25 ml conc.  $\text{HNO}_3$ . Five to 10 drops ca. 0.5%  $\text{H}_2\text{SiF}_6$  are added to each sample to facilitate solution. The samples are warmed until solution is completed and then 5 ml conc.  $\text{HNO}_3$  are added to each beaker and enough water to bring the volume to 25-35 ml. About 0.5 g of potassium metaperiodate is added to each sample and the solutions boiled for 5-10 min. After cooling, the solutions are transferred to 50 ml volumetric flasks, diluted to the calibration mark and mixed thoroughly. Transmittancies are determined using a Coleman Universal spectrophotometer and the concentration of manganese obtained by comparison with a calibration curve.

The calibration curve is obtained in the following manner. A stock manganous nitrate solution is prepared by dissolving 100 mg of electrolytic manganese in 20 ml of 1:10  $\text{HNO}_3$  and diluting to one liter giving a solution containing 1 mg Mn/ml. Eight solutions containing from 0-0.1 mg Mn per 50 ml are then prepared, and 15 ml of 2:1  $\text{HNO}_3$  are added to each. The solutions are heated to boiling, 0.5 g  $\text{KIO}_4$  added, to each and boiling continued 5-10 min. After cooling, the solutions are heated to boiling, 0.5 g  $\text{KIO}_4$  added, to each and boiling continued 5-10 min. After cooling, the solutions are diluted in 50 ml volumetric flasks and mixed. The transmittancies are determined and the data obtained is plotted on semi-log paper giving the calibration curve.

ANL

A 20 ml aliquot of the sample solution described under the chromium procedure is added to a 50 ml beaker along with 1 drop of 1%  $\text{AgNO}_3$ . The solution is diluted to 25 ml, 0.2 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  are added, and the solution is quickly brought to a boil over a small burner. After cooling at room temperature for about one min, and then in an ice bath, the solution is transferred to a 25 ml volumetric flask using a wash solution which has been oxidized as above. The solution is diluted to 25 ml, transferred to 5 cm cells and read at 525 m $\mu$  against a blank on the reagents.

FMI

A sample containing from 0.025 to 0.30 mg of manganese is dissolved in a 250 ml beaker with 7 ml of  $\text{HNO}_3$  and 5 to 10 drops of 0.05 M HF. After gentle warming to remove the last traces of the oxide, 10 ml of boric acid are added and warming continued for 10-15 min. The solution is diluted to 50 ml and heated to boiling. One g of solid  $\text{KIO}_4$  is added and boiling continued for 5 min. The solution is cooled to room temperature, diluted to 100 ml, and read in a 5 cm cell at 525 m $\mu$ . For a reference solution, a sample is carried through all the procedure but the addition of  $\text{KIO}_4$  is omitted.

NBL

A 5 g thorium metal sample is weighed and transferred into a 250 ml beaker. Forty ml of conc.  $\text{HNO}_3$  are added and the sample is warmed on a steam bath. If no reaction occurs, or when any reaction has ceased, a few drops of 1:100 HF are added. The sample is digested on a steam bath until completely dissolved, adding more hydrofluoric acid if necessary to continue the reaction. The solution is evaporated to volume of about

25 ml, then 10 ml  $\text{HNO}_3$ , approximately 0.5 g  $\text{KIO}_4$ , and a few glass beads are added. The solution is boiled for 5 min, cooled to room temperature, and diluted to 50 ml in a graduated cylinder. The light transmittancy of the solution is measured against a reagent blank in a Beckman spectrophotometer, at 525  $\text{m}\mu$  in 5 cm cells. The concentration of manganese present is read from a transmittancy concentration curve, and the ppm calculated. The curve is prepared by developing the color in solution containing 0, 20, 40, 60, 80, and 100  $\mu\text{g}$  of manganese, according to the above procedure and plotting the curve on semi-log paper.

MOLYBDENUMFMT

A sample containing from 0.02 to 0.12 mg of molybdenum is weighed, and dissolved in a 250 ml beaker in 10-15 ml of  $\text{HNO}_3$  and 5-10 drops of 0.05 M HF. When the action ceases, 15 ml of  $\text{HClO}_4$  are added, and the solution fumed to remove HF and  $\text{HNO}_3$ . After cooling somewhat, 20-25 ml  $\text{H}_2\text{O}$  are added. From a burette, 5 ml of sodium thiocyanate solution (5 g/100 ml  $\text{H}_2\text{O}$ ) are introduced, and the mixture transferred to a 100 ml separatory funnel. The beaker is rinsed with 10 ml of stannous chloride solution (250 g  $\text{SnCl}_2$ , 200 ml conc.  $\text{HCl}$ , 1200 ml  $\text{H}_2\text{O}$ ) which is added from a burette, and the solution is transferred to the funnel. The beaker is rinsed with a final wash of 20 ml of butyl acetate, which is added to the funnel. After one min of vigorous shaking, the aqueous layer is separated and discarded. In succession, 5 ml sodium thiocyanate solution and 15 ml of stannous chloride solution are added to the funnel. Again, after shaking, the aqueous layer is discarded. The butyl acetate layer is placed in a 50 ml volumetric flask together with two 10 ml butyl acetate rinses. The flask is diluted to mark and read in a 1 cm cell at 470 m $\mu$ . For a reference solution, a butyl acetate extract is used containing all the reagents used in the analysis.

NICKELAMES

A 4 g sample of thorium metal is dissolved in conc. nitric acid containing a trace of fluosilicic acid. If any chloride is present it is necessary to evaporate the solution to fumes with perchloric acid. Aliquots of the sample solution containing 0.4 g of thorium are transferred to 100 ml volumetric flasks. To the sample solution 10 ml of 50% citric acid aqueous solution, and 15 ml of conc. ammonium hydroxide are added and the solution is allowed to cool to room temperature. Ten ml sat. bromine water are added, followed by the immediate addition of 10 ml of 1, 2-cycloheptanedionedioxime (sat. aqueous solution). The solution is diluted to mark, and the absorbancy is measured vs. a reagent blank 35  $\pm$  10 min after the addition of the last reagent. A Beckman DU spectrophotometer is used with matched Corex cells at 443 m $\mu$  and a slit width of 0.03 mm.

ANL

A 15 ml aliquot of the sample solution described under the chromium procedures is transferred to a 25 ml volumetric flask. Two ml 45 % potassium nitrate and 10 drops H<sub>2</sub>SO<sub>4</sub> + 10 drops saturated bromine water are added. The solution is cooled in an ice bath, neutralized and made ammoniacal with ammonium hydroxide. Ten drops of 1% dimethylglyoxime in ethanol are added, the solution diluted to volume, and read at 520 m $\mu$  against a reagent blank. The amount of nickel present is obtained from a previously prepared transmittance-concentration curve.

BMT

A sample containing from 0.005 to 0.050 mg of nickel is weighed, and dissolved in a 250 ml beaker in 15 ml of  $\text{HNO}_3$  and 5-10 drops of 0.05 M HF. After warming, 10 ml  $\text{HClO}_4$  are added and the solution heated to fumes. When cool, 30-35 ml  $\text{H}_2\text{O}$  and 5 g citric acid/g of sample are added. The solution is made slightly ammoniacal, and 2 ml of dimethylglyoxime (1% in alcohol) are added. The solution is placed in a separatory funnel and three extractions are made with 2-3 ml portions of chloroform, shaking for one-half min each time. The combined extracts are mixed with 5 ml of 1:50  $\text{NH}_4\text{OH}$  solution and the chloroform is run into another separatory funnel. The water layer is shaken with 2 ml chloroform and the latter combined with the washed extract.

The chloroform solution is shaken for one min with two portions of 0.5 N HCl each of 5 ml volume. The acid washes are transferred to a 25 ml volumetric flask. Five drops of sat. bromine water are added followed by conc.  $\text{NH}_4\text{OH}$  until the color of bromine is destroyed plus an excess of 3 or 4 drops. Finally, 0.5 ml of 1% dimethylglyoxime in ethanol is added and the solution diluted to volume with water. The reading is made in a 1 cm cell at 460 m $\mu$  using water as a reference.

ORNL

A colorimetric method with diethyl dithiocarbamate is used, and measurements made with a Beckman DU spectrophotometer.

NITROGENAMES

The thorium metal to be analyzed is cleaned by placing it in 8 N  $\text{HNO}_3$ , adding 6 mg of sodium fluosilicate and warming the mixture until the metal surface is bright. The sample is removed, washed with water and dried. A 5 g sample is cautiously dissolved in 50 ml of 6 N HCl containing 6 mg of sodium fluosilicate, warming if necessary to effect complete solution. The solution is quantitatively transferred to a 100 ml volumetric flask, diluted to volume and a 20 ml aliquot is pipetted into the Kjeldahl apparatus described by Ma and Zuazaga\*. Twenty ml of a

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\* Ma, T.S., and G. Zuazaga, Ind. Eng. Chem., Anal. Ed., 14, 280-282 (1942)

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boric acid indicator solution described below is divided between the 125 ml Erlenmeyer receiving flask and the vapor trap. Fifty ml of a 35% NaOH solution are added to the thorium chloride solution and the alkaline solution is steam distilled. Fifty ml of condensate are collected in the boric acid indicator solution. The receiving flask is lowered, the top of the condenser is washed with distilled water and the ammonia is titrated with 0.01 N HCl using a micro-buret.

The boric acid indicator solution is made by pipetting 10 ml "methyl purple" indicator solution as purchased from Fleischer Chemical Company, Washington, D. C., into a boric acid solution made by dissolving 20 g reagent grade crystalline boric acid into 800 ml of redistilled water. The boric acid indicator solution is diluted to a liter and mixed. A blank is run by pipetting 10 ml of this solution into the receiving



flask along with enough redistilled water to give the same volume as a distillate titration. The titration is done with 0.01N HCl. If an appreciable volume of hydrochloric acid is required, the boric acid indicator solution is adjusted with 0.01 N HCl so that less than 0.1-0.2 ml HCl is required to titrate the blank.

#### ANL

A one gram sample is dissolved in hydrochloric acid and a trace of hydrofluoric acid. To the clear solution, which is washed into the nitrogen distillation apparatus, are added 20 ml of 33% NaOH. The distillate is collected in 5 ml of 2% boric acid and titrated with 0.01 N HCl.

#### BMI

A 0.5 to 1.0 g sample is transferred to a 50 ml Griffin beaker and treated with 25 ml of 1:1 HCl. After the rapid hydrogen evolution has subsided, the solution is heated without boiling until the bubbling stops. Eight to 10 drops of  $\text{HBF}_4$  are added to assist in solution of the sample. The cool solution is transferred to a Parnas-Wagner nitrogen apparatus with a minimum of wash water (If the blank titration exceeds 0.3 ml of 0.008 N HCl the water should be distilled over sodium hydroxide and potassium permanganate using the middle third portion of condensate). Twenty-five ml of 38% NaOH are added and the ammonia distilled. (The NaOH solution contains 0.5 g deVarda's alloy per 1.5 lb. NaOH. It is prepared by dissolving this amount of NaOH in 2000 ml  $\text{H}_2\text{O}$ , adding the alloy, and boiling down to a volume of 1800 ml). A few drops of sulfuric acid in the steam generator eliminates a possible blank from the steam.

Ten ml of condensate are collected in a 50 ml Erlenmeyer flask containing 5 drops of indicator and 10 ml of 0.16%  $\text{H}_3\text{BO}_3$  (4%  $\text{H}_3\text{BO}_3$  should be used if sample contains 0.1%  $\text{N}_2$  or more). The flame should be adjusted so that 5 min after the condenser head gets hot, 10 ml of condensate have been collected. When distilling a sample, the discharge end of the condenser should be immersed for 3 min, and brought above the boric acid solution for the remaining 2 min.

The reagent blank is titrated with 0.008 N HCl (0.08 N acid for samples over 0.1% nitrogen) to the first appearance of pink. With the blank for comparison, the sample is titrated to the same color. A Machlett or similar type burette calibrated in 0.01 ml divisions is recommended. The indicator is made by dissolving 0.0166 g of methyl red and 0.0834 g of bromcresol green in 100 ml of neutral alcohol.

The vacuum fusion method for nitrogen is included in the oxygen vacuum fusion procedure.

#### HOR

A 0.5 g sample is weighed and placed in a 250 ml beaker with 40 ml  $\text{H}_2\text{O}$ . Ten ml conc. HCl are added slowly under cool conditions until gas evolution has ceased. The sample is then heated just to dryness, and after cooling, 10-15 ml HCl are added and the sample taken to dryness again. The original fine gray precipitate should change to a fine yellow or buff color. The procedure of adding HCl and taking to dryness is repeated until solution is effected. The hydrochloric acid volume should be adjusted to 4-5 ml.

A blank of 4-5 ml HCl, 10 ml 50% NaOH, and 5-10 ml  $\text{H}_2\text{O}$  is run through the Micro-Kjeldahl apparatus. A ten minute distillation from

the first drop is sufficient. The receiver contains 5 ml of 2% boric acid plus 3 drops of methyl red. The sample is treated in the same manner as the blank and is titrated with 0.01 NHCl.

#### KAPL

A standard Kjeldahl analysis is performed. The sample is dissolved in hydrochloric acid with a trace of hydrofluoric acid. Boric acid is added to tie up the hydrofluoric. After steam distillation, the nitrogen content is determined colorimetrically.

Nitrogen is also determined by a vacuum fusion analysis of both the thorium chips and solid metal. Recovery factors are not determined.

#### MIT

A 2 g sample is dissolved in 25 ml 6 N HCl which contains 2 drops of 48% HF and the ammonia is steam distilled from a sodium hydroxide solution and titrated.

#### NLC

A one gram sample is dissolved with 20% HCl and a few drops of fluosilicic acid. The sample is digested at low heat for 4 hr, a solution of sodium hydroxide added, and a distillation made with a conventional type of Kjeldahl apparatus. The distillate is collected in boric acid solution which is titrated with a standard solution of hydrochloric acid.

#### NBL

A one gram sample of chips is weighed and transferred into a micro-Kjeldahl flask. The flask is placed in cold water and 10 ml of

20 % HCl are added. When the reaction has subsided, the flask is removed from the water and two drops of conc. hydrofluosilicic acid are added to dissolve the precipitate. The solution is boiled for 10 min.

While the sample is dissolving, the steam generator is filled with redistilled water and the distillation flask is steamed out for 15 min with the steam trap outlet open. The trap is closed and steam distilled for 5 min. The steam trap is then drained. (Figure 4).

Seven ml of boric acid-indicator solution is poured in a 30 ml Erlenmeyer flask which is placed under the condenser with the tip under the solution. (The indicator consists of 5 parts bromcresol green solution to one part of methyl red solution. Both solutions are 0.1% alcoholic solutions. Sixteen ml of indicator are added per liter of 2% boric acid solution.) To the distillation flask 15 ml of 37.5% NaOH are added, and the funnel washed down with redistilled water. The sample solution is added, followed by three 5 ml washes of redistilled water. The solution is distilled for 3 min collecting 20-25 ml of distillate. The receiving flask is lowered and distillation continued for one min more. Titration is done with 0.0100 N HCl to the appearance of a pink end point. A blank is run prior to sample determinations. No more than 0.02 ml of acid should be required for the blank.

#### ORNL

Using the vacuum fusion method, the residual gas pressure after removal of condensable gases, etc., is assumed to be due to nitrogen.

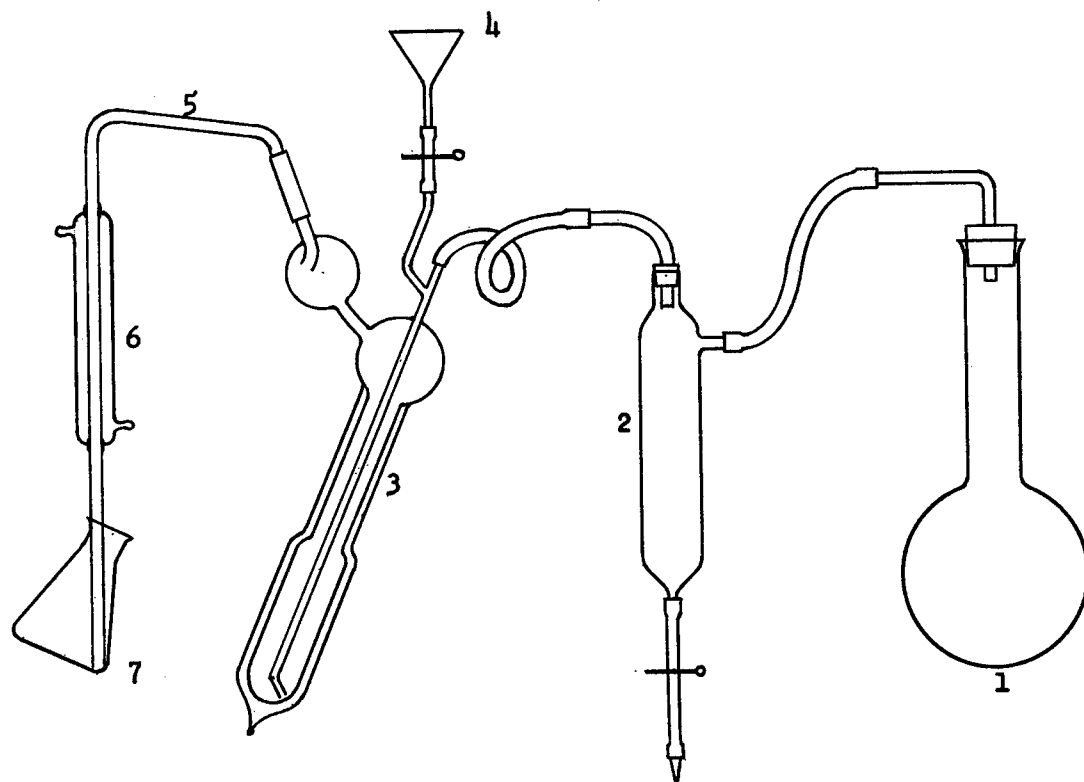


FIGURE 4. KJELDAHL DISTILLATION APPARATUS

1. Steam Generator
2. Steam Trap
3. Distilling Flask
4. Introduction Funnel
5. Silver Tube Condenser
6. Condenser Jacket
7. Erlenmeyer Flask

## OXYGEN

### AMES

A 2-5 g sample of chips is cleaned by treating with dil.  $\text{HNO}_3$  containing a small amount of fluosilicic acid to remove any surface oxide. The sample is washed with water and dried. After weighing it is transferred to a 250 ml beaker and treated with 8 ml of 1:1  $\text{HCl}$ , 2 ml of conc.  $\text{HNO}_3$ , and 10 ml of 70-72%  $\text{HClO}_4$ . The beaker is covered with a watch glass and allowed to stand until the vigorous evolution of hydrogen has ceased. It is then heated on a hot plate and evaporated to copious fumes of perchloric acid for 10 min. After cooling to room temperature, any material adhering to the watch glass is washed into the beaker and the solution diluted to about 50 ml. The solution is filtered using S&S Blue Ribbon Filter Paper. The precipitate is washed with ten 20 ml portions of water (It is necessary to cover the wet filter paper with ammonium oxalate crystals to avoid a rapid deflagration or ignition due to the remaining traces of  $\text{HClO}_4$ ). The residue is dried and ignited to constant weight using a platinum crucible in a muffle at  $1100^\circ\text{C}$ . The perchloric acid insoluble thus obtained is taken as a measure of the combined oxygen in the thorium metal.

### ANL

Oxygen is determined by melting 0.1 g samples of thorium in a platinum bath contained in a graphite crucible which is heated to about  $1930^\circ\text{C}$  by induction heating. The evolved  $\text{CO}$  resulting from the interaction of oxygen in the sample with carbon from the crucible is swept by a stream of purified argon through a tube of Schutze reagent for conversion to  $\text{CO}_2$ . The  $\text{CO}_2$  is condensed out of the argon, isolated,

and measured by its pressure at room temperature. This is an application of a method developed by W. G. Smiley of the Los Alamos Laboratory.

#### BMI

The oxygen is determined by the Ames solution technique described by Rasmussen, and also by the vacuum fusion procedure.

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S. W. Rasmussen, "Tentative Method for Oxygen in Thorium Metal as HCl Insoluble," CC 2694, Feb. 23, 1945

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The vacuum fusion analyses are carried out in a tin bath in a graphite crucible at 1750°C. Approximately 4 g of graphite chips contained in the crucible are degassed at 2350°C until a satisfactory furnace blank is obtained at 1750°C. The temperature is lowered to 1200°C and about 20 g (for a 5 g sample) of C.P. tin are dropped into the crucible. The temperature is then slowly raised to 1750°C to keep spattering of the tin to a minimum. After the tin has been degassed, the sample is dropped and the evolved gases are collected for one hr. The gases are then analyzed for oxygen, nitrogen, and hydrogen in a modified Orsat apparatus.

#### HOR

The acid insoluble residue method is employed.

#### KAPL

Oxygen is determined by the vacuum fusion method.

#### MIT

A two g sample of chips is placed in a 150 ml Pyrex beaker, and 10 ml of 6 N HCl containing one drop of 48% HF are added. After complete solution of the metal, 10 ml of H<sub>2</sub>O and 25 ml of 0.85 M H<sub>3</sub>BO<sub>3</sub> are added and the solution filtered on a 9 cm "blue" S&S filter paper

and washed with hot 2% HCl solution. The paper is ignited and the residue weighed. The oxygen content is calculated assuming the residue to be thorium oxide.

#### NLC

A one gram sample is boiled for 4 hr in 300 ml of 6N HCl. Helium is constantly bubbled through the solution during this period. The sample is cooled to room temperature and filtered on #42 Whatman paper. Subsequently, the residue is washed with 1:10 HCl, and ignited in a platinum crucible at 800°C. The residue is then reweighed and the concentration of insoluble material determined.

#### NBL

A 1-1.5 g sample of chips is treated with 300 ml of 6N HCl free of dissolved oxygen (Nitrogen is bubbled through 1:1 HCl for 5-10 min using a bubble dispenser). The sample is boiled gently for at least 4 hr. If the solution is faintly yellow, boiling is continued until the yellow color disappears. More 6N HCl is added to maintain approximately the same volume. The sample is cooled, filtered through #42 Whatman filter paper, and washed with 1:10 HCl. The precipitate is ignited at 1000°C for one hour and weighed.

#### ORNL

Vacuum fusion is used. Samples are dropped into a gas-free iron bath at 1900°C in a graphite crucible. The oxygen is converted to CO, then CO<sub>2</sub>, and measured as such.



RARE EARTHSANL

A sample aliquot containing 0.2 g of thorium is converted to chloride by evaporating to dryness twice after the addition of 5 ml of HCl and followed by evaporation to dryness twice after the addition of 5 ml of H<sub>2</sub>O. Thorium chloride is taken up in 1.56 m.e. HCl, transferred to a 250 ml separatory funnel, diluted to 50 ml, and extracted for 1 min with 100 ml of 0.2 M thenoyltrifluoroacetone (TTA) in benzene. After the phases are separated, the aqueous phase is re-extracted with 50 ml TTA to remove the last traces of thorium. The aqueous solution is evaporated to 1.0 ml from which 0.1 ml aliquots are analyzed spectrographically using the copper spark method.

BMI

After a cellulose column separation, the rare earths are determined spectrographically.

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Center, E. J., et al., "The Determination of Rare Earths in Thorium,"  
BMI-260, May 15, 1952.

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NBL

Sufficient 1:1 HNO<sub>3</sub> and a few drops of dilute hydrofluoric acid are used to carefully dissolve a 50 g sample of chips. After dissolution, the solution is boiled, and gradually raised to 140°C. It is then stirred until crystallization takes place and it is almost cool. The sample is ready for partial separation of thorium by the cellulose column technique.

The column is prepared as follows: A small amount of glass wool is placed in the bottom of the glass column, and about  $5\frac{1}{2}$ " of powdered cellulose (Whatman Ashless Powder for Chromatograph) placed on the wool. A disc of paper cut from a Whatman "accelerator" that fits snugly in the column is placed over the cellulose, and slight pressure is employed to pack the column.

Twenty-five ml conc.  $\text{HNO}_3$  are added by pipette to 200 ml ether with stirring to avoid loss of ether. Sixty ml of this acidified ether are run through the column. The balance is poured over the sample and stirred slowly. Immediately, another batch of ether- $\text{HNO}_3$  is prepared. The solvent on the sample is transferred to the column and the sample covered with the new batch of acidified ether. This technique is repeated until the sample is reduced to an aqueous solution. This solution is treated with one more batch of acidified ether which is then passed through the column. The ether- $\text{HNO}_3$  solvent is forced through the column using a controlled flow of air through a rubber tube supplied with a screw clamp to control the pressure. The solvent is passed through the column at a rate of about 20 ml/min.

When the meniscus from the last batch of acidified ether has just dropped below the level of the top of the cellulose column, the receiver is changed and 100 ml of 1:7  $\text{HNO}_3$  is added. After this has passed through the column, three more 100 ml portions are similarly added. The column is given a slight excess pressure after the last portion has passed through. The receiver beaker containing the "elute" is placed on a steam bath and a small quantity of the ether evaporated. The sample is ready for final thorium separation.

The solution is made ammoniacal by adding an excess of 25 ml  $\text{NH}_4\text{OH}$ . The sample is set on the steam bath until the precipitate settles. After filtering on #40 Whatman paper, the precipitate is dissolved with hot 1:1 HCl. Ten g of  $\text{NH}_4\text{Cl}$ , ca. 0.1 g sodium sulfate, and one or two drops of methyl red indicator are added. Then sufficient ammonium hydroxide is added until a precipitate is first formed. This is then dissolved with a few drops of 1:1 HCl.

The solution is placed on the hot plate and a 5% hexamine solution added in one ml portions until a precipitate forms plus 3 ml in excess. After 5 min on the hot plate, the precipitate is collected on #40 Whatman paper, and then dissolved with hot 1:1 HCl, collecting in the precipitating beaker.

A second and third hexamine precipitations are made and the filtrates combined. Twenty-five ml  $\text{NH}_4\text{OH}$  are added and the solution warmed on the hot plate until the precipitate has coagulated. Paper pulp is added and the solution filtered through #40 Whatman paper. The precipitate is dissolved with hot 1:1 HCl. The filtrate is collected in a 250 ml beaker and three more hexamine precipitations are carried out, omitting the addition of ammonium chloride. The filtrates are combined in a 400 ml beaker, treated with 25 ml of  $\text{NH}_4\text{OH}$ , and boiled 3-5 min. After cooling to room temperature, the precipitate is filtered through a #40 Whatman paper and dissolved with hot 1:1 HCl, collecting the filtrate in a small platinum dish. This solution is evaporated to dryness on the steam bath.

The residue is treated with 5 ml of  $\text{H}_2\text{O}$ , followed with 5 ml saturated oxalic acid solution, and digested on the steam bath for 5 min. Then 10 ml of  $\text{H}_2\text{O}$  are added, the sample removed from the steam bath and allowed to stand overnight.

The precipitated oxalates are filtered through a 5.5 cm #40 Whatman paper, washed with 2% oxalic acid, and then the precipitate and paper ignited in a tared platinum crucible for 40 min at 600°C.

The oxides are transferred to a small platinum dish, treated with 10 ml 1:1  $\text{HNO}_3$  and ca. 2 mg NaF, and placed on the steam bath. After about 5 min the oxides should be completely dissolved. An amount of titanium solution is added so that the ignited oxide contains about 1%  $\text{TiO}_2$ . The sample is removed from the steam bath and one drop of methyl red is added. The solution is made ammoniacal, with about 5 ml of  $\text{NH}_4\text{OH}$  in excess, and then digested on the steam bath for 5 min. After filtering through a 5.5 cm #40 Whatman paper, the precipitate and paper are transferred to the original crucible and ignited for 30 min at 600°C, and then at 1000°C for 10 min. The crucible is placed in a desiccator, cooled to room temperature and weighed. The rare earth content is then computed after correcting for the titanium added.

#### ORNL

The cellulose column is used as described in EMI-260, followed by spectrographic analysis.

SILICONMIT

A 2.5 g sample of chips is dissolved and the thorium precipitated as described under the MIT determination of aluminum. An aliquot solution equivalent to 0.25 g thorium, is transferred to a polyethylene beaker for color development. The pH is adjusted to 2.5 with 20%  $(\text{NH}_4)_2\text{CO}_3$  solution; 5 ml of 10% ammonium molybdate are added and the pH adjusted to 2.3 with 1:1 HCl. After standing 10 min, 25 ml of 17% sodium sulfite solution are added with thorough stirring using a platinum rod. After 10 min, 10 ml of 40% ammonium tartrate solution are added. The solution is transferred to a 200 ml volumetric flask, diluted to mark with water and mixed. The optical density is measured in 5 cm cells at 710 m $\mu$  with distilled water in the comparison cell. A proper reagent blank correction is made. In the case of the blank, boric acid is added to complex the small amount of hydrofluoric acid present.

TITANIUMAMES

A 5 g sample is dissolved in 1:1  $\text{HNO}_3$  containing a small amount of fluosilicic acid, transferred to a 100 ml volumetric flask and diluted to volume. A 20 ml aliquot is transferred to a 25 ml volumetric flask and 6 drops of 28%  $\text{H}_2\text{O}_2$  are added, followed by mixing and dilution to mark. The color develops immediately and is read at 410 m $\mu$  using a Coleman Universal Spectrophotometer, Model 11. A 5 cm cell is used for faint solutions and a 1 cm cell for darker solutions.

A standard curve is prepared by dissolving 0.739 g of  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  in 40 ml of hot conc.  $\text{H}_2\text{SO}_4$ , diluting to a liter and mixing.

Five, 10, 20, 30 and 40 ml aliquots of this solution, containing 10 g Ti/ml, are pipetted into 100 ml volumetric flasks. Four ml of conc.  $\text{H}_2\text{SO}_4$  are added to each and the solutions diluted to 80 ml with distilled water. Four ml of 28%  $\text{H}_2\text{O}_2$  are added, the solutions diluted to volume and mixed. Transmittancies are determined before using water as a reference. The standard curve is plotted on semi-log paper.

URANIUMAMES

A sample of 10 g, weighed to the nearest .01 g is dissolved in 100 ml of 8 M  $\text{HNO}_3$  to which 1 ml of dil.  $\text{H}_2\text{SiF}_6$  has been added. After dissolution, the solution is evaporated to about 10-15 ml on a hot plate. It is then removed to a steam bath and evaporated to dryness. The residue is dissolved in 15 ml of  $\text{H}_2\text{O}$  and filtered through a sintered glass filter of medium porosity. The filter is washed with 5 ml of  $\text{H}_2\text{O}$  which is added to the sample solution.

The thorium nitrate solution is placed in a 100 ml separatory funnel containing 25 ml of redistilled diethyl ether. The mixture is shaken vigorously for 5 min and the phases separated. The aqueous phase is returned to the funnel and 25 ml of ether are added. After shaking for 5 min the aqueous phase is discarded and the ether phases combined. Twenty ml of distilled water are added to the ether in a 150 ml beaker, and the ether is evaporated using a low temperature hot plate. The liquid is then shaken gently and evaporated to 5-10 ml.

The solution is transferred to a 25 ml volumetric flask and the pH adjusted to  $0.7 \pm 0.3$  with 2 ml of 1 N HCl. Two ml of 10%  $\text{SnCl}_2$  solution (50 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 50 ml conc. HCl, filtered through a fine porosity sintered glass filter and diluted to 500 ml with  $\text{H}_2\text{O}$ ) are added and the flask is shaken vigorously. This amount of stannous chloride will compensate for 2 mg of interfering ferric ion. Ten ml of 8 M  $\text{NH}_4\text{SCN}$  (filtered through a fine porosity sintered glass filter, and the pH adjusted to 7 with ammonium hydroxide) are added and the solution immediately diluted to 25.00 ml with water, followed by shaking. Readings are made against

a reagent blank 5 min  $\pm$  30 sec after the thiocyanate is added, using a Beckman DU spectrophotometer (equipped with a hydrogen lamp for use in the ultraviolet). Data are taken at 380 m $\mu$  using 5 cm cells. A standard curve is prepared using the given procedure and known amounts of uranium added to a solution of pure thorium. The blanks are prepared at the same time as the samples as they deteriorate with time. (A stable blank may be prepared using 0.15 mg chromic chromium per ml of solution. It should be checked from time to time with fresh blanks.)

#### ANL

A one gram sample is dissolved with HCl + HNO<sub>3</sub> and a small amount of ammonium fluoride. The solution is diluted to 250 ml and a 10 ml aliquot evaporated to dryness on a steam bath. Then 50 ml H<sub>2</sub>O and sufficient nitric acid are added so that the pH is one after the addition of thenoyltrifluoroacetone (TTA). Three extractions of 100, 50, and 50 ml are made with 0.2 M TTA in benzene. The aqueous layer is evaporated to 2 ml and submitted for the fluorometric determination of uranium.

#### BMI

The fluorometric method is used following a preliminary separation the cellulose column.

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Center, E. J., "Topical Report on the Direct Micro Determination of Uranium Using a Modified Fluorophotometer." AECD-3006, June 30, 1948.

Center, E. J., et al, "Topical Report on Analytical Control of Thorium, Uranium, and Rare Earths in the Processing of Monazite Sands," JDS-BMI-193, May 31, 1949.

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#### KAPL

The quenching effect of thorium upon the uranium fluorescence is reduced by hexone extraction of uranium from aluminum nitrate.



Distribution ratios of uranium and thorium between hexone and aluminum nitrate are given for two sets of conditions:

<u>Condition</u>	<u><math>E \frac{O}{a} U</math></u>	<u><math>E \frac{O}{a} Th</math></u>
1.9 M $Al(NO_3)_3$ 0.2 M $HNO_3$	7.5	0.22
1.6 M $Al(NO_3)_3$ 0.0 M $HNO_3$	7.5	0.20

To remove 99.84%-99.92% of the thorium and effect a 60% recovery of uranium the following procedure is followed:

Two hundred and fifty lambda of 2 molar thorium solution are added to 400λ of saturated (2.5M) neutral aluminum nitrate and extracted with 500λ of hexone. The hexone phase is then scrubbed with three consecutive fresh 600λ portions of neutral 1.6 M aluminum nitrate (400λ neutral aluminum nitrate plus 200λ  $H_2O$ ). The hexone is then analyzed fluorometrically (cf. KAPL-102, p. 572) for uranium and corrected for the 60% recovery.

#### ORNL

The uranium is extracted using hexone with aluminum nitrate as the salting agent. This is followed by the standard sodium fluoride fluorometric procedure.

ZINCAMES

A sample of chips weighing less than 10 g (depending on the zinc content) is weighed into a 600 ml beaker, covered with water, and 50 ml of conc. HCl carefully added. After the vigorous reaction has ceased, ca. 5 mg of  $\text{Na}_2\text{SiF}_6$  are added and the solution boiled until the black residue has dissolved. The solution is evaporated to 20 ml; 25 ml of 2 molar sulfosalicylic acid, and 4 ml of a 0.5% gelatin solution are added. The solution is treated with 20 ml  $\text{NH}_4\text{OH}$  and stirred until all the precipitate has dissolved. The pH is adjusted to  $8.5 \pm 0.2$  and the solution transferred to a 100 ml volumetric flask. After dilution to volume and mixing, 10 ml are placed in the polarographic cell and purged for 15 min with nitrogen to remove any residual oxygen from the solution. The polarogram is then recorded using a Sargent Polarograph, Model XXI.

Calibration is done by the standard addition method. A known amount of zinc is added to another sample of the same size and the sample treated in the same manner as the unknown. The concentration of zinc added, divided by the difference in diffusion currents of the two polarograms gives the factor by which the diffusion current of the unknown is multiplied to determine the zinc content in the unknown. When sulfosalicylic acid is used to complex the thorium, the zinc half wave potential occurs at -1.05 v. versus the saturated calomel electrode.

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Patterson, J. H., & C. V. Banks, Analytical Chem., 20, 897, (1948)

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BMI

A sample containing 5-25  $\mu\text{g}$  of zinc is weighed and placed in a 250 ml beaker. Ten to 15 ml  $\text{HNO}_3$  and a drop of fluosilicic acid are added, followed by gentle heating to effect solution. The solution is boiled to incipient separation of salts, then diluted to 50 ml with water.

Twenty-five ml of 40% (w/v) ammonium citrate (5 g Th require 75 ml citrate), 1 ml of 20% (w/v)  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , and 1 ml of 12.5% (w/v)  $\text{Na}_2\text{S}_2\text{O}_3$  are added. The pH is adjusted to 5.0-5.5 with ammonium hydroxide. The sample is extracted with dithizone (10-20 mg/l) in carbon tetrachloride using 5 ml portions. Extraction is complete when a fresh portion of dithizone remains green after 2 min of vigorous shaking. The combined carbon tetrachloride extracts are washed with 50 ml of 0.02 N  $\text{HCl}$  by shaking for 2 min. The carbon tetrachloride layer is discarded.

The aqueous layer is treated with 1 ml of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution and 1 ml of  $\text{Na}_2\text{S}_2\text{O}_3$  solution as above. The pH is adjusted to 5.0-5.5 and extraction repeated until a final addition remains an unchanged green.

The combined carbon tetrachloride extracts are brought to a 50 ml volume and washed with 50 ml portions of 0.4% (w/v)  $\text{Na}_2\text{S}$  solution until the sulfide solution no longer turns yellow. (If an emulsion forms at this point, it may usually be broken by adding a "pinch" of fine  $\text{KCl}$  crystals). The washed zinc dithizonate is filtered through a dry paper and read in a 1 cm cell at 535  $\text{m}\mu$  and 0.01  $\text{m}\mu$  slit against a carbon tetrachloride reference. Blanks are carried through the whole procedure. All reagents (except  $\text{HNO}_3$ ,  $\text{NH}_4\text{OH}$ , and  $\text{Na}_2\text{S}$ ) are extracted with dithizone to keep the blank as low as possible.

ORNL

The polarographic method is employed.

## SECTION IV. SPECTROGRAPHIC PROCEDURES

AMES LABORATORY

The carrier distillation method is used for the determination of boron, cadmium, and zinc; and the conducting briquet technique is employed for the determination of aluminum, beryllium, calcium, iron, magnesium, manganese and zirconium.

Oxide Preparation

For routine analytical purposes, the thorium metal is converted to the oxide by ignition of fine turnings or millings in a muffle for about 3 hr. Synthetic standards, however, are prepared by adding standardized solutions of the impurities to solutions of thorium nitrate, precipitating the thorium by adding an excess of ammonium hydroxide, evaporating the slurry to dryness and igniting to the oxide.

Carrier - Distillation

The following experimental conditions are being used for the determination of boron, cadmium and zinc.

Sample:	100 mg charge (94% ThO <sub>2</sub> , 6% AgCl) blended in agate mortar, dried in oven at 100 °C for several hr, and weighed into lower (anode) electrode, tamped, and vented. Prepared electrodes are kept in dessicator until excited.
Electrode Assembly:	Upper (cathode) - 1/8 in. diam, boron free graphite

Lower (anode) - 1/4 in. diam, boron free graphite, 9-1/2 mm deep cavity, wall thickness of 3/64 in.

spectrograph: Bausch and Lomb Littrow - Quartz optics

Plates: S. A. #1

Slit: 25 microns

Source: 10 amp, 220 v d.c. arc

Exposure: Duration of stable arc: + 5 sec for boron and cadmium; 25 sec for zinc

Analysis Lines: B 2497.9 Å  
Cd 2288.0 Å  
Zn 3302.6 Å

Concentration Ranges: B 0.1 - 2 ppm  
Cd 0.1 - 5 ppm  
Zn 20-800 ppm

In determining boron content, correction must be made for interference of thorium lines.

#### Conducting Briquet Technique

This technique can be used for the quantitative determination of all impurities for which adequate sensitivity can be achieved. Pertinent experimental details of this method, as it is used at the present time, are as follows:

Spectrograph: Jarrell-Ash 21 ft grating spectrograph

Upper Electrode: Flat end graphite rod, 1/8 in. diam

Lower Electrode: Cylindrical pellet, 1/4 in. diam prepared as follows: thorium metal turnings ignited

at 750 °C for 3 - 4 hr. The resulting thorium oxide is ground thoroughly in a WC mortar and mixed with an equal weight of natural flake graphite (National Carbon Co. Sp-2) and briquetted with an ARL briquetting press at 7000 lbs. Normally a mixture of about 300 mg of oxide and 300 mg of the graphite are pelleted.

**Excitation Source:**

ARL Multisource

Capacitance - 50 microfarads

Resistance - 15 ohms

Inductance - 400 microhenries

Initiator - Low Power

Phase angle - 60°

Primary Current- 18.5 - 19 amp

Voltage - 910 v

**Exposure Time:**

60 sec

**Slit Width:**

45 microns

**Emulsion:**

SA # 1

**Spectral Region:**

2300 - 4200 Å

**Filter:**

Glass for 3600 - 4200 Å

**Order:**

Second

**Intensity Modulation:**

Step filter for obtaining stepped spectrograms suitable for determination of all impurities.

**Emulsion Calibration:**

4 amp d.c. iron arc, step-sector, preliminary curve method

The line pairs employed for the determination of the more important impurities are summarized in Ames Table 1.

The Si 2516.123 line may have a weak thorium line interference. However, if the contribution to the total intensity is entirely assigned to residual impurity, the concentration equivalence is only about 20 ppm. The aluminum, calcium, and nickel lines possess very weak thorium line interference; correction for these interferences are made in the analytical curves.

For visual estimation of certain impurities, the following line pairs are used for reporting the impurities as "less than " the values indicated. At the concentrations indicated in Ames Table 2, the respective line pairs have an intensity ratio of one, and by observing that the intensity ratios are less than one, the concentrations can be reported as "less than" the established values.



AMES TABLE 1

## Line Pairs Used for the Conducting Briquet Technique

Line Pair	Concentration Range
<u>Fe 2599.396</u> Th 2603.59	20 - 600 ppm
<u>Be 3130.42</u> Th 3141.85	10 - 500 ppm
<u>Mg 2802.695</u> Th 2816.08	20 - 600 ppm
<u>Al 3961.527</u> Th 3923.81	10 - 600 ppm
<u>Ca 3933.666</u> Th 3895.35	20 - 600 ppm
<u>Si 2516.123</u> Th 2534.68	30 - 600 ppm
<u>Ni 3012.004</u> Th 2972.379	20 - 600 ppm
<u>Zr 3496.210</u> Th 3491.901	100 - 1200 ppm
<u>Zr 3496.210</u> Th 3491.579	250 - 4000 ppm

AMES TABLE 2

## Line Pairs Used for Visual Analyses

Line Pair	Concentration Range
<u>Si 2516.123</u> <u>Th 2517.97</u>	less than 50 ppm if intensity ratio is less than 1
<u>Mn 2605.688</u> <u>Th 2603.59</u>	less than 20 ppm if in- tensity ratio is less than 1
<u>Ca 3933.666</u> <u>Th 3931.22</u>	less than 50 ppm if in- tensity ratio is less than 1
<u>Mg 2802.695</u> <u>Th 2800.25</u>	less than 20 ppm if in- tensity ratio is less than 1

### ARGONNE NATIONAL LABORATORY

The carrier distillation technique is employed using gallium oxide.

The elements determined in the oxide sample are: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, silver, sodium, strontium, tin, titanium, vanadium, wolfram and zinc.

#### Procedure

Twenty-five mg of sample are ground with 2-1/2 mg of gallium oxide in an agate mortar for 10 min. This mixture is put into a 1/4 in. graphite electrode having a crater 5/32 in. in diam by 1/4 in. deep. Prior to burning the filled electrode, it is placed in an oven set at 100 °C for at least 15 min. This heat treatment causes the sample to burn uniformly by driving off any moisture accumulated in preparation. The sample is partially burned using a National Spectrographic Arc Source. The spectrum is photographed using a Bausch and Lomb Quartz Littrow Spectrograph. The sample spectrum is compared visually with standards using a Dietert Projection Comparator.

Three samples are necessary for a complete analysis. One sample is exposed from 5 in. - 45 in. at 15 amp in position (8) which covers 2200 Å to 2800 Å. The second sample is exposed from 5 in. - 45 in. at 15 amp in position (6) which covers 2400 Å to 3300 Å. The third sample is exposed from 5 in. - 30 in. at 15 amp in position (2) which covers 3300 Å to 7800 Å. An S. A. I plate is used for positions (8) and (6) and a I-N plate for position (2). Both plates are developed in D-19 for 3 min in a tank.

For the analysis of impurities in thorium metal, it is necessary to convert the metal to the oxide. This is done by igniting the shavings of thorium metal in a platinum dish placed in a muffle furnace set at  $900^{\circ}\text{C}$  for 2 hr.

#### Preparation of Standards

The matrix material is supplied in the form of thorium nitrate by the Lindsay Light and Chemical Co. This is converted to thorium oxide by heating about 100 gm in a platinum dish over a Meker burner for 2 hr. The material is then ignited in a muffle furnace set at  $900^{\circ}\text{C}$  for 4 hr.

A standard is ground to contain 10,000 ppm of each element. Portions of this top standard are diluted with matrix material and ground so that a group of standards are obtained ranging from 10,000 ppm to 0.1 ppm in steps of 10, 5, 2 and 1. Two sets of standards are prepared. One set contains elements of refractory nature. The second set contains elements that volatilize easily.

#### Reproducibility

A 200 ppm standard containing refractory elements and a 200 ppm standard containing the less refractory elements are exposed 10 times on the same plate. Results have indicated that the average deviation is never more than  $\pm 20\%$ . The maximum deviation, however, has approached 100%.

#### Lower Limits of Analysis

Table 1 shows the spectrum lines used for analysis and their lower limits of detection.

ANL TABLE 1

Analysis Lines Used and Lower Limits of  
Detection for Impurities in Thorium Oxide

Element	Wave Length (Å)	Lower Limit (ppm)
Ag	3280.6	0.1
Al*	3092.7	20
As	2780.2	10
B	2497.7	0.1
Ba	6141.7	5
Be	3130.4	0.1
Bi	3067.7	1
Ca*	4226.7	20
Cd	2288.0	0.5
Co	2521.4	5
Cr	2843.3	1
Ca*	3247.5	20
Fe*	2490.7	5
K	7664.9	20
Li	6707.8	1
Mg*	2852.1	10
Mn*	2794.8	1
Mo	3132.6	10
Na*	5889.9	5
Ni	3101.5	5
P	2553.2	20

ANL TABLE 1 (contd.)

Element	Wave Length (Å)	Lower Limit (ppm)
Pb	2833.0	1
Sb	2598.1	1
Si*	2881.6	50
Sn	2839.9	5
Sr	4077.7	50
Tl	3234.5	20
V	3110.7	20
W	2831.4	100
Zn	3345.0	20

\* Lower limit controlled by residual impurity in matrix material.

BATELLE MEMORIAL INSTITUTEConversion of Thorium and Thorium Salts to Thorium Dioxide

Thorium in the form of turnings, chips or pieces of metal, is washed with ethyl ether to remove oil or grease, pickled in 25% nitric acid at 90 to 100 °C for about 20 min, washed free of nitric acid with distilled water, and dried by rinsing with acetone. The sample of metal, now free of surface contamination, is ignited in platinum ware in a furnace at 850 to 1000 °C for several hours until it is converted to thorium oxide. Thorium hydroxide, thorium peroxide, thorium oxalate, thorium iodate, thorium chloride, thorium perchlorate and thorium nitrate are readily ignited to thorium oxide at 900 to 1000 °C. Thorium sulfate or thorium peroxide, precipitated from a sulfuric acid solution, must be ignited at 1200 to 1300 °C to produce thorium oxide. Usually, the thorium compounds are heated slowly over a Meker burner at first, then ignited at the full temperature of the burner, and then put in a furnace to complete the ignition to thorium oxide at the higher temperature. The ignition is usually carried out in platinum ware. For the iron, copper and boron determinations, a standard Globar-type furnace containing a fused silica liner is used.

Preparation of Carrier and Sample

4.85 g AgCl and 0.15 g Bi<sub>2</sub>O<sub>3</sub> are thoroughly mixed in a polished agate mortar. This mixture is the carrier material. 0.470 g ThO<sub>2</sub> sample and 0.030 g of carrier are mixed in an agate mortar for 15 to 20 min, then transferred to a clean, labeled glass vial and held for the analysis. The sample mixed in an agate mortar is used for all analyses except silicon.

0.100 g charges for each standard and a blank are weighed and transferred to a deep-crater, thick-walled, pure graphite electrode. Two 0.100 g

charges of each sample are weighed and transferred to the electrodes, as in the case of the standards. Two exposures are made for each sample analysis.

The charge in each electrode is tamped and, holding the electrode with a pair of small tweezers, the bottom of the electrode is gently tapped on the electrode block to jar loose material on the side walls of the electrode down into the electrode. Any material resting on the top of the electrode is brushed off with a clean camel's hair brush. A vent hole is punched in each charge with a needle and the exposures are made. The loaded lower electrode is the anode: the 1/8 in. upper electrode is the cathode.

#### Preparation of Carrier and Sample for Silicon Analysis

The same proportions of silver chloride and bismuth oxide as the carrier mixture are mixed in a sapphire mortar instead of an agate mortar.

0.282 g  $\text{ThO}_2$  sample and 0.018 g of carrier are then mixed for 15 to 20 min in a sapphire mortar. The mixture is transferred to a clean, labeled glass vial and held for analysis for silicon. The procedure is the same as for the other elements.

#### Preparation of Standards

Materials:  $\text{AgCl}$  - Mallinckrodt, Analytical Reagent Grade.

$\text{Bi}_2\text{O}_3$  - Bakers Analyzed, C. P. Grade.

$\text{ThO}_2$  - Very pure material obtained from New Brunswick Laboratory

Other Chemicals - The best purity obtainable

Standards containing the necessary elements as impurities and covering the desired range are dry mixed. Table 1 gives the impurities which are added and the range which is covered. The carrier is added to the standards before they are mixed so that the complete mixing operation can be carried



out at one time. Each standard is mixed and ground in the agate mortar for about 2 hr, then stored in a clean, labeled glass vial.

#### Standards for Silicon and Indium in Thorium Oxide

Special standards are prepared for silicon and indium in thorium oxide. The impurities are added as solutions, dried with an infrared lamp, and ignited at 900 °C in a furnace, the carrier added, and then ground in a sapphire mortar for about 2 hr. These standards are stored in clean, labeled glass vials.

#### Equipment and Exposure Conditions

Spectrograph - ARL 1.5 Meter Grating

Source - ARL Multisource

Film - Eastman Kodak Spectrum Analysis No. 1

Spectral Regions - Second Order, 2000 Å to 4600 Å (Instrument has 2 cameras)

Slit - 20 microns

Filter at Slit, No. 7 - 12% Transmission Filter

Filters before Film - Mg 2802 Å, Si 2881 Å, Cu 3274 Å

Diaphragm at Film - about 1 mm

Electrode Gap - 5 to 6 mm

Preburn - No preburn

Exposure - 45 sec

Excitation - 12.5 to 13 amp, rectified pulsating d.c. arc

Spectrogram Record - On Film Envelope

Exposure Cycle - The electrode clamps are cleaned off, the electrodes inserted and adjusted to proper position, and the arc started with the igniter. The upper electrode is ad-

BMI TABLE 1 - COMPOSITION OF STANDARDS

Standard No.	Impurities Added to Thorium Oxide, ppm												
	Al	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Ge	In*	K
1	320	3.2	320	16	320	6.4	160	320	160	640	160	160	52
2	160	1.6	160	8	160	3.2	80	160	80	320	80	80	26
3	80	0.8	80	4	80	1.6	40	80	40	160	40	40	13
4	40	0.4	40	2	40	0.8	20	40	20	80	20	20	6.5
5	20	0.2	20	1	20	0.4	10	20	10	40	10	10	3
6	10	0.1	10	0.5	10	0.2	5	10	5	20	5	5	1.5
7	5	0.05	5	0.25	5	0.1	2.5	5	2.5	10	2.5	2.5	0.75
Blank	<10	<0.05	-	-	-	-	-	-	<1	<2	-	-	-

Standard No.	Impurities Added to Thorium Oxide, ppm											
	Mg	Mn	Mo	Ni	P	Pb	Sb	Si*	Sn	V	W	Zn
1	80	160	320	320	640	160	160	320	160	320	2000	640
2	40	80	160	160	320	80	80	160	80	160	1000	320
3	20	40	80	80	160	40	40	80	40	80	500	160
4	10	20	40	40	80	20	20	40	20	40	250	80
5	5	10	20	20	40	10	10	20	10	20	125	40
6	2.5	5	10	10	20	5	5	10	5	10	62.5	20
7	1.25	2.5	5	5	10	2.5	2.5	5	2.5	5	31	10
Blank	-	<2	-	<5	-	<1	-	-	-	-	-	-

\* This is a special set of standards prepared in a sapphire mortar.

justed to maintain a 5 to 6 mm gap throughout the exposure. An automatic timer cuts off the exposure at 45 sec. The plate is racked. The electrodes are removed, the charge is dumped into the scrap container, and the electrodes are discarded. The cycle is then repeated on the next sample.

Film Development - ARL Rocking-Type Film Developer

Developer - D-19, 3 min at  $21\frac{1}{3}$  °C

Short Stop - Acetic Acid, 20 to 30 sec

Fix - F-5, 1 to 2 min

Washing and Drying - The film is washed for 2 min in film washer, rinsed in distilled water, the excess water removed with a sponge, and the film dried for 4 min or until dry.

#### Exposure Conditions for Very Low Concentrations of Boron and Cadmium

The conditions are similar to those for the other elements, with the exposure time changed and the amount of light falling on the slit increased. Exposure time is 30 sec.

Filter No. 4 - 34% Transmission

Filter 2810 Å - Internal Standard Line

#### Photometry

Densitometer readings are obtained from selected element lines and the adjacent film background. Readings are also made of selected bismuth lines as internal standard lines and their adjacent background. After converting to intensity readings, and making background corrections, if necessary, inten-

sity ratios are computed.

Table 2 lists the wavelengths of the element, the standard lines which are used, and the usual detection limit of each element.

#### A Concentration Method for the Determination of Molybdenum in Thorium

This method is based on the co-precipitation of molybdenum sulfide with copper sulfide as carrier. A relatively large sample is utilized, and the molybdenum is separated from the thorium. Molybdenum is detected and determined in the range 0.1 ppm to 10 ppm by this method.

Stock solutions include: 6N  $\text{H}_2\text{SO}_4$ , 0.3N  $\text{H}_2\text{SO}_4$ , 1% Cu solution, 0.005% Mo solution in  $\text{H}_2\text{SO}_4$ .

#### Chemical Procedure

Two g Th metal are dissolved in a 250 ml beaker using cover glass with 40 ml 1-1 HCl. To assist in the solution of the sample, a few drops of a dilute solution of hydrofluosilicic acid are added from time to time. During the process of heating the solution, 10 ml conc.  $\text{HNO}_3$  are added. The solution is then evaporated to low volume. Ten ml conc.  $\text{HNO}_3$  are again added and the solution evaporated nearly to dryness. The sample is redissolved in distilled water.

Two ml conc.  $\text{H}_2\text{SO}_4$  are added to the sample which is then heated to decompose the nitrate and convert the sample to the sulfate. Thorium sulfate is soluble in cold 0.2 to 0.3 N  $\text{H}_2\text{SO}_4$ . Two g of thorium metal as a sulfate will dissolve in 200 ml 0.2 to 0.3 N  $\text{H}_2\text{SO}_4$ .

BML TABLE 2 - ANALYTICAL LINES AND DETECTION LIMITS

Element	Wavelength Å	Internal Standard	Wavelength Å	Usual Detec- tion Limit, ppm
Al	3944	Bi	2989 3rd Order	5
Al	3961.5	Bi	2989 3rd Order	
B	2496.778	Bi	3076.7	0.05
Ba	4554 1st Order	Bi	3076.7	1
Be	3130	Bi	3076.7	0.1
Ca	3179	Bi	3076.7	
Ca	3933.7	Bi	2989 3rd Order	
Ca	3968.5	Bi	2989 3rd Order	1
Ca	4226.7	Bi	2989 3rd Order	
Cd	2288	Bi	2810	0.1
Cr	4274.8	Bi	2989 3rd Order	5
Co	2521.4	Bi	3076.7	1
Cu	3247	Bi	3076.7	0.5
Cu	3274	Bi	3076.7	0.5
Fe	3020.489	Bi	3076.7	
Fe	3020.640	Bi	3076.7	1
Ge	2651.18	Bi	3076.7	
Ge	2651.57	Bi	3076.7	1
In	3256.09	Bi	3076.7	5
K	7664.9	None	-	
K	7698.98	None	-	2
Li	6103.6	None	-	
Li	6707.8	None	-	

BMI TABLE 2 - ANALYTICAL LINES AND DETECTION LIMITS (con'd)

Element	Wavelength Å	Internal Standard	Wavelength Å	Usual Detec- tion Limit, ppm
Mg	2802	Bi	3076.7	1
Mn	2594	Bi	3076.7	1
Na	5889.9	None	-	
Na	5895.9	None	-	1
Ni	3050	Bi	3076.7	1
Ni	3054	Bi	3076.7	
P	2554.9	Bi	3076.7	
Pb	2833	Bi	3076.7	2
Si	2516	Bi	3076.7	
Si	2881	Bi	3076.7	3
Sb	2598	Bi	3076.7	5
Sn	2863	Bi	3076.7	2
V	3185	Bi	3076.7	5
Zn	3302	Bi	3076.7	30
Zn	3345	Bi	3076.7	30

The solution is neutralized with ammonia, using Universal pH indicator to test the pH. The pH is adjusted to 6-7.

Some precipitation of thorium occurs, but this goes back into solution when the proper acidity is attained later. 12.5 ml of 6N  $\text{H}_2\text{SO}_4$  are added and the volume of the solution adjusted to approximately 250 ml. The solution is now 0.3N with respect to sulfuric acid.

One ml of 1% Cu solution is added and the sulfides of copper and molybdenum are precipitated in the cold solution by passing a gentle stream of hydrogen sulfide into it for 20 min. The sulfides are allowed to settle. The copper and molybdenum sulfides are filtered with a No. 42 Whatman filter paper. The filter is washed 10 times with 0.3 N  $\text{H}_2\text{SO}_4$ . The filter is drained thoroughly and the paper with the sulfides on it is transferred to a porcelain crucible. This is dried on a hotplate, transferred to a muffle furnace at 450 ° C and ignited. Overnight ashing is convenient for this step. The oxides of copper and molybdenum are transferred to a 3/32 in. deep spectrographic electrode.

Four standards and a blank should be prepared and put through the same process as the sample. The standards are prepared by adding molybdenum from a stock solution to molybdenum free thorium.

It may be noted that thorium sulfate free from molybdenum may be prepared by putting a quantity of thorium through the process outlined above for co-precipitation of molybdenum.

#### Spectrographic Procedure

Film - Spectrum Analysis No. 1

Spectrograph - ARL 1.5 Meter Grating

Excitation - 10 amp d.c. multisource

Exposure - Both regions 30 sec

Slit - 20 microns

Filter - No. 2. 70% before the slit

Development - D-19, 3 min at  $21\frac{1}{3}$  °C

Molybdenum Analysis Line, 2780.5 Å

Copper - Internal Standard Line, 2783.5 Å



KNOLLS ATOMIC POWER LABORATORY

The thenoyltrifluoroacetone method (cf. KAPL 749, p. 118) is adapted to thorium. Thorium nitrate solution is diluted to 0.25 molar nitrate (determined by titration of the sample with sodium hydroxide to the phenolphthalein end point), and extracted five times with equal volumes of 0.5M TTA in xylene. Thorium removal is followed by "thoron" colorimetrically. The raffinate is evaporated to the equivalent of 0.6 g Th/0.5 ml and 0.06 g Th/0.5 ml, and submitted for spectrographic analysis.

Standards are prepared by dissolving the impurity elements in 2N HNO<sub>3</sub>. Using the standard series indicated in Table 1, a set of standard curves are obtained. The analytical lines used to obtain transmission readings are given in Table 2, along with the detection limits corrected for sample size.

The concentrated sample is arced five times, the dilute sample six times, and the concentrated sample diluted ten-fold and arced six times. For the dilute samples, the detection limit values are poorer by a factor of ten. It was observed that for both dilute samples impurity concentrations of a number of the elements were too low to be read accurately. Averages of the two dilute samples and the concentrated sample are made for those elements yielding readable values in the dilute runs.

An indication of the spectrographic reproducibility of the analysis is given in Table 3, by comparison of columns (2), (3), and (4). An example of the effect of chemical treatment of the standard of column (2) is shown in column (5). In column (6), the apparent concentration of each element in the blank sample is given.

KAPL TABLE 1

PPM FOR ELEMENTS IN STANDARD SERIES EQUIVALENT TO FIVE MG SAMPLE

Be	.1	.2	.4	1	2	4	10
Cu	.5	1	2	5	10	20	50
Bi, Mn, V	1	2	4	10	20	40	100
Mg, Ni, Pb, Sn	5	10	20	50	100	200	500
Al, Ca, Cr, Zn	10	20	40	100	200	400	1000
Na	21.2	42.5	85	212	425	850	2120
B	20	40	80	200	400	800	2000

KAPL TABLE 2

## ANALYTICAL LINES AND DETECTION LIMITS

Element	Wavelength Å	Detection Limit (ppm) (.6 g Th sample size)
Al	3082.2 3092.7	1
Bi	3067.7	0.5
Ca	3158.9	3.3
Cr	2835.6	1.7
Cu	3247.5	0.1
Mg	2852.1 2795.5	0.4
Mn	2576.1	0.5
Ni	3002.5 3414.8	1
Pb	2833.1	4
Sn	3175.1	1.7
V	3184.0	0.8
Zn	3345.0	5

KAPL TABLE 3APPARENT CONCENTRATION OF BLANK AND ONE STANDARD  
(ppm)\*

(1) Element	(2) Actual Standard Concentration	(3) Apparent Conc. 1st Plate	(4) Apparent Conc. 2nd Plate	(5) Standard TTA Treated	(6) Apparant Blank Conc.
Al	100	90	112	110	< 1
Bi	10	8.5	8	7	< 0.5
Ca	100	120	122	148	4.4
Cr	100	90	94	100	1.7
Cu	5	4.5	5	8.8	0.13
Mg	50	39	35	45	< 0.5
Mn	10	6.7	8.1	9.8	< 0.3
Ni	50	50	50	54	< 1
Pb	50	50	< 50	45	< 3.5
Sn	50	38	41	66	< 1.7
V	10	12	11.3	12	< 1
Zn	100	84	68	112	< 3.3

\* all results corrected for sample size

Fyrex equipment is used in the chemical procedure, hence, no analysis of boron, silicon or sodium is reported. Beryllium values are not reported because the lines are too dark to read accurately.

#### NATIONAL LEAD COMPANY

The thorium metal samples are converted to the oxide by ignition in a muffle furnace which is held at approximately 700 °C. Test pieces are contained in covered quartz crucibles. The resulting thorium oxide is analyzed by the carrier distillation procedure of Scribner and Mullin, which is described on the following pages under New Brunswick Laboratory.

#### Preparation of Standards

The thorium oxide that is used as matrix material is derived from the ignition of thorium nitrate supplied by the Lindsay Light and Chemical Company. Blank determinations are made on this material, portions are "spiked" with known quantities of contaminants and the analyses are conducted under the same conditions as used in the analysis of the billet.

NEW BRUNSWICK LABORATORY

The general procedure provides for the determination of the following elements by the carrier distillation procedure\*: aluminum, arsenic,

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\* Scribner, B. F., and Mullin, H. R., J. Research Nat'l Bur. Standards, 37, 379, (1946).

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beryllium, bismuth, boron, cadmium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, silicon, silver, tin, vanadium and zinc. It is also possible to analyze for alkali elements by this method, if a special run is made on the spectrograph.

Preparation of Oxide Sample

Thorium metal turnings or chips are first degreased with carbon tetrachloride and allowed to air dry on filter paper. To prepare a thorium metal slug for analysis, a 1.0 - 1.5 g sample is sawed off with a hack saw and its surface is cleaned by filing or scraping. The sample of turnings is placed on a bar in a platinum dish and 15 - 20 ml  $\text{HNO}_3$  plus a few drops of 1:100 HF are added. The dish is placed on a hot plate at low heat until the metal has dissolved and is evaporated to dryness. The metal is ignited over a burner until the nitrate is entirely decomposed, and is then placed in a muffle furnace and the ignition is completed at 900 °C for 2 hr.

Procedure

The sample is reground for 3 - 5 min in a clean agate mortar until a very fine powder is obtained. The sample is replaced in the original vial. 735 mg of the ground thorium oxide are weighed out and placed in a clean agate mortar. Fifteen mg of gallium oxide containing 1% Cr as chromic oxide are

added and this is ground for 3 min. Portions of the thorium oxide standards are treated in the same manner, but 4.90 g of standard mixed with 0.10 g of gallium oxide are used. (Prior to the analysis of samples, a reference plate is prepared and photographed for each set of standards, following the conditions described for the routine analysis.)

A 100 mg charge of the thorium oxide, gallium oxide mixture is weighed out and placed in a 9/32 in. deep crater pure graphite electrode\*. Duplicate

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\* Scribner, B. F., and Mullin, H. R., J. Research Nat'l Bur. Standards, 37, 379, (1946).

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portions of each sample are taken for analysis. A full plate listing consists of six sample charges and two comparison standard charges with a complete sample record on the plate envelope. Duplicate sample portions are placed on different spectrum plates when possible.

The charge is tamped in each electrode by holding the electrode with a pair of tweezers while gently tapping the electrode against the electrode block. With the special needle punch a vent hole is made in the electrode charge, making sure that the vent hole goes through the sample into the electrode itself. The sample is now ready for exposure at the spectrograph.

#### Exposure Conditions

Spectrograph:	Baird
Setting:	2.4 (2100 - 3530 Å)
Cassette:	979.2
Rotation:	997.8
Position:	498.7

Electrode Stand:	Arc focused on grating
Filter:	None
Slit:	25 microns
Line Mesh:	Full open
Grating aperture:	3/4 in.
Sector:	Steps 1 to 5 where 1 is 360° Step ratio is 1 to 2
Upper Electrode:	1/8 in. pointed cathode
Lower Electrode:	Sample electrode set firmly on pedestal which is 1/8 in. tapered rod extending 1/2 in. above electrode clamp
Electrode Gap:	4 mm adjusted by projection of electrode images on screen in electrode housing
Excitation:	Rectifier d.c. current is adjusted to 14 amp with electrode clamps. Shorted current during exposure cycle is approximately 12.5 amp.
Pre-arc:	5 sec
Exposure:	35 sec
Plate:	SAI
Plate Processing:	2 min D-19 at 70 °F, 15 sec in 3% acetic acid shortstop, 2 min rapid fixer hypo, 2 min running water wash, dried on plate dryer.
Photometry:	Densitometer lines as shown in the follow- ing tabulation. The indicated intensity ratios and then the impurity concentration are determined after making the necessary plate corrections shown by the standard values.

Cr	2762 Å
Cu	3273
Fe	2599
Ni	3050
Pb	2833
Sn	3175
Zn	3345

The analytical curves for copper, lead, tin  
and zinc are obtained by plotting Log I



impurities vs. concentration while the curves for iron and nickel are plotted Log I impurities/Cr vs. concentration. After densitometry of the sample plate, it is removed to viewing box and visual examination is made for remaining impurities by comparison with standard plates.

#### Analysis of Rare Earth Concentrates

The spectrographic examination of the rare earth concentrate is at present limited to qualitative analysis. The rare earths obtained from thorium samples are generally of a cerium-lanthanum matrix which differs spectrographically from the yttrium matrix common to uranium samples. Therefore, direct comparison of these samples against yttrium base standards gives only approximate results.

Some indication of the amount of the various rare earths present in the concentrate is obtained if the average value is used for the qualitative designation and the concentration is then calculated from the total rare earths present as determined chemically.

#### Procedure

For each sample, a 0.5 mg portion is weighed on the 50 mg Roller-Smith balance as accurately as possible, and 2.5 mg of graphite powder is added to the sample in the pan. The materials are mixed on the pan and the mixture is transferred to a 1/32 in. cup in a 1/4 in. pure graphite electrode. (See electrode reference under general procedure.) The standards used are prepared in the same manner. A complete exposure record is kept on the plate envelope. The sample is now ready for exposure on the spectrograph.

NBL TABLE 1

## COMPOSITION OF STANDARDS

Impurities added to thorium oxide as ppm in the oxide

Standard	A	B	C	D	E	F
Al	500	200	100	50	20	10
As	500	200	100	50	20	10
Ca	500	200	100	50	20	10
Fe	500	200	100	50	20	10
Mg	500	200	100	50	20	10
Mn	500	200	100	50	20	10
Mo	500	200	100	50	20	10
P	500	200	100	50	20	10
Si	500	200	100	50	20	10
Sr	500	200	100	50	20	10
Ti	500	200	100	50	20	10
V	500	200	100	50	20	10
Zn	500	200	100	50	20	10
Zr	500	200	100	50	20	10
Be	50	20	10	5	2	1
Bi	50	20	10	5	2	1
Co	50	20	10	5	2	1
Cr	50	20	10	5	2	1
Cu	50	20	10	5	2	1
Ni	50	20	10	5	2	1
Pb	50	20	10	5	2	1
Sn	50	20	10	5	2	1
Sb	50	20	10	5	2	1
Ag	5	2	1	0.5	0.2	0.1
B	5	2	1	0.5	0.2	0.1
Ge	5	2	.1	0.5	0.2	0.1
In	5	2	1	0.5	0.2	0.1

The standards are prepared by adding the required amount of impurity to the pure thorium oxide to make standard A. Each succeeding standard is prepared by diluting the previously prepared standard with a calculated amount of thorium oxide base material.

NBL TABLE 2

## WAVELENGTHS OF IMPURITY ELEMENTS CHECKED IN THORIUM OXIDE ANALYSIS

Element	Wavelength, Å	Element	Wavelength, Å
Ag	3280.7	Mg	2802.7 2778.3
Al	3082.2	Mn	2798.3
As	2288.1 2349.8	Mo	3132.6
B	2496.8 2497.7	Na	3303.0
Be	2348.6	Ni	3050.8
Bi	3067.7	P	2553.3 2535.7
Cd	2288.0	Pb	2833.1
Co	3453.5	Sb	2598.1
Cu	3247.5 3274.0	Si	2435.2 2881.6
Ge	3039.1	Sn	3175.0
Fe	2599.4	V	3183.4 3184.0 3185.4
In	3256.1	Zn	3345.6

NBL TABLE 3

## WAVELENGTHS OF ELEMENTS FOR USE IN ANALYSIS OF RARE EARTH CONCENTRATES

Element	Wavelength, Å	Element	Wavelength, Å
Al	3961.5	Nd	3951.2
Ca	3933.7 3968.5	Pr	3908.4 4008.7
Ce	4012.4	Sc	3353.7
Dy	3405.66	Si	2881.6
Er	3264.8	Sm	3634.3
Eu	3972.0	Tb	3324.4
Gd	3100.5	Th	2870.4 4019.1
Ho	3416.5	Tm	3131.3
La	3988.5	Y	3664.6
Lu	2900.3	Yb	3289.4

NBL TABLE 4

## ELEMENT SENSITIVITIES IN THORIUM OXIDE

Element	Estimated Sensitivity (ppm)	Element	Estimated Sensitivity (ppm)
Ag	0.05	Li	0.3
Al	5	Mg	0.5
As	3	Mn	1
B	0.1	Mo	3
Ba	8	Na	2
Bi	0.2	Ni	0.5
Ca	3	P	20
Cd	0.05	Pb	0.2
Co	4	Sb	1-2
Cr	4	Si	5
Cu	0.1	Sn	1
Fe	0.5	V	15
K	5	Zn	5

Exposure Conditions

Spectrograph:	Baird
Setting:	3.5 (2000 - 4100 Å)
Cassette:	975.7
Rotation:	996.7
Position:	497.6
Electrode Stand:	Arc focused on grating
Filter:	None
Slit:	25 microns
Line Mesh:	Full open
Grating aperture:	1/4 in.
Sector:	Steps Step ratio is 1 to 2
Upper Electrode:	1/8 in. pointed cathode
Lower Electrode:	Sample electrode is set firmly on pedestal which is 1/8 in. tapered rod extending 1/2 in. above electrode clamp.
Electrode Gap:	4 mm as adjusted by projection of electrode image on screen in electrode housing.
Excitation:	Same setting is used as for general procedure
Pre-arc:	None
Exposure:	40 sec
Plate:	SAI
Plate processing:	2 min D-19 at 70 °F, 15 sec in 3% acetic acid short stop, 2 min rapid fixer hypo, 2 min running water wash, dried on plate dryer
Plate examination:	Plate examined for wavelengths listed in report Table in qualitative range

THE OAK RIDGE NATIONAL LABORATORY

The following spectrochemical method is used for aluminum, beryllium, nickel, copper, chromium and manganese. The metal is dissolved in nitric acid containing a trace of ammoniumfluosilicate, and is extracted from 5N  $\text{HNO}_3$  solution with tributylphosphate. The remaining aqueous phase is analyzed spectrographically by the porous cup method. For beryllium, and in certain other cases, it is unnecessary to remove thorium, as its lines do not interfere (in this case, with Be 2348 Å).

For iron, the metal is dissolved in hydrochloric acid containing a faint trace of ammoniumfluosilicate. The iron is separated from thorium by anion exchange column, stripped and determined spectrographically by the porous cup method.

In the analysis of boron, the sample is roasted at 640 °C, mixed with silver chloride and exposed by the pyroelectric method, using external standards. The thorium oxide used for standards is first freed of boron by pyroelectric flushing.

Rare earths: the thorium sample is dissolved and run through a cellulose column as described in BMI 260: it is then column ignited, the residue dissolved and run through the cellulose column again to remove the residual thorium. The rare earths are determined in solution by the porous cup technique, and the results corrected for losses during manipulation by use of europium tracer (carrier free).

The lower limits of detection for impurities in the oxide sample are given in ORNL Table 1.

ORNL TABLE 1

Lower Limits of Detection for Impurities  
in Thorium Oxide.

Element	Lower Limit
Al	0.05
B	0.5
Be	0.002
Ca	a0.1
Cd	a1
Ce	a2
Cr	0.1
Cu	0.05
La	0.02
Mn	0.1
Nd	a2
Ni	0.2
Ti	0.2



## SECTION V. DANGER COEFFICIENT TEST

A danger coefficient test was performed to roughly check the thermal neutron absorption cross section of the impurity elements in the Ames billet, A-520. Crystal bar thorium metal made by the iodide process at Battelle Memorial Institute was used as a reference material. This material contains a very low concentration of impurity elements and hence is suitable as a reference specimen.

In order to perform the danger coefficient test it is necessary that the two samples are as identical in shape as possible. Hence the test specimens were cast and machined to the following specifications, calculated to minimize self-shielding and end effects:

Weight:	1000 $\pm$ 5 g
Diameter:	0.500 $\pm$ 0.010 in.
Length:	ca. 26.7 in. as determined by the restrictions on weight and diameter
Surface:	Machined smooth

The test was conducted in the CP-2 reactor located at Argonne National Laboratory by Mr. C. Egger of ANL.

## Results & Calculations

### A. Danger Coefficient Test

The Ames metal was found to have an apparent thermal absorption of  $0.068 \pm 0.010$  cm<sup>2</sup> more than the Battelle iodide metal. This result is corrected for a 0.9 g greater mass of the Ames sample.

### B. Thermal Absorption of Impurities in the Ames Metal

The thermal absorption is calculated based on the average of the analytical results. Only those elements with  $\frac{\sigma_{ai} M_i}{A_i}$  greater than one are itemized:

<u>Element</u>	<u>ppm</u>	<u><math>\sigma_a</math></u>	<u><math>\frac{\sigma_{ai} M_i}{A_i}</math></u>
B	0.4	750	27.73
Cd	0.1	2400	2.14
Cl	(15)	31.6	13.35
Co	(<2)	34.8	< 1.18
Dy	(<1)	1100	< 6.77
Eu	(<0.3)	4500	< 8.88
Fe	60	2.43	2.61
Gd	(0.35)	44,000	98.15
H	(10)	0.330	3.27
In	(<5)	190	< 8.28
Li	<1	67	< 9.65
N	60	1.78	7.62
Nd	6	44	1.83
Ni	27	4.5	2.07
Sm	(<0.5)	6500	< 21.61
Zr*	(400)	1.66	7.20
Others	-	-	4.67

227.01

\*includes effect of 2.5 wt % Hafnium

$$\sigma_{a_{imp.}} = \sum_i \frac{\sigma_i M_i}{A_i} \times \frac{.6023}{1000}$$

$$\sigma_{a_{imp}} = 0.137 \text{ cm}^2$$

If the "less than" values are omitted then:

$$(\sigma_{a_{imp}})_{min.} = 0.103 \text{ cm}^2$$

### C. Thermal Absorption of Impurities in BMI Iodide Metal

The BMI analysis of the iodide thorium is given below together with the calculated thermal absorption:

<u>Element</u>	<u>ppm</u>	<u><math>\sigma_a</math></u>	<u><math>\frac{\sigma_{\text{Mi}}}{\text{Al}}</math></u>
C	100	.0045	0.04
N	30	1.78	3.81
B	0.4	750	27.73
Cd	<0.1	2400	< 2.14
Li	< 5	67	< 48.27
Dy	< 5	1100	< 33.85
Eu	< 1	4500	< 29.60
Gd	< 1	44,000	< 280.43
Sm	< 5	6500	< 216.09

$$\sigma_{\text{aimp}} = \frac{641.96}{0.387} \text{ cm}^2$$

If the "less than" values are omitted then:

$$(\sigma_{\text{aimp}})_{\text{min}} = 0.019 \text{ cm}^2$$

### Conclusions

The difference in absorption between the Ames thorium and the Battelle material is very small. It may be noted that the change of .068 cm<sup>2</sup> in absorption is equivalent to about 0.4 ppm of gadolinium. In order to calculate this absorption difference, the analysis of the highly absorbing impurity elements must be known with considerably more accuracy than presently known.

If a calculation is made, however, as is exhibited in B and C, a better correlation is observed if the "less than" values are neglected. The first result below is negative because of the higher detection limit given for the rare earths and lithium in the iodide thorium.

Ames Metal cm <sup>2</sup>	Iodide Metal cm <sup>2</sup>	$\sigma_{imp}$ cm <sup>2</sup>	
		calc.	experimental
.137	.387	-0.250	0.068 $\pm$ .01
.103	.019	0.084	

In summary, the only conclusion that can be drawn from the danger coefficient test in view of the high detection limits for many of the important absorbers, is that there are no gross errors or omissions of highly absorbing impurity elements in the Ames thorium metal.

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